EVERYONE'S BOOK OF THE WEATHER

BY

A. FRANCON WILLIAMS, F.R.S.G.S.

WITH NUMEROUS DIAGRAMS

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PREFACE

In these days of wireless reports, meteorological charts and forecasts, journeys by aeroplane or airship, scientific farming and plantation work and the like, interest in the weather is becoming more and more widespread, and a knowledge of atmospheric phenomena is useful as well as fascinating.

The object of the present work is to present the facts of meteorology to the general reader in a popular form, and to show how observers equipped with quite simple instruments can find pleasure as well as profit in the study of weather conditions.

A. FRANCON WILLIAMS.

Kalimpong, Bengal,
December, 1922.

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THE FUNDAMENTAL CAUSES OF WEATHER

Some Magic Districts.

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Now I am going to show that in reality we ought not to think so much of the *sea* in these wonderful places as of the *weather* that is experienced there. These magic regions owe their interest to special conditions of what is spoken of as **weather.** But before we can understand what weather means we must know something of the atmosphere.

The Atmosphere.

The atmosphere is the air which envelops the earth. It is a mixture of gases, the most common being nitrogen and oxygen.

Air is a fluid—that is, it flows from one place to

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CHAPTER I

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The Atmosphere.

The atmosphere is the air which envelops the earth. It is a mixture of gases, the most common being nitrogen and oxygen.

Air is a fluid—that is, it flows from one place to

another. It has no definite shape, and can move about easily when disturbed. The disturbances of the atmosphere are the fundamental causes of weather.

How the Atmosphere is Disturbed.

Although the atmosphere is invisible, yet its constituents are as real in substance as the solid and liquid matter which we see. The atmosphere has weight just as other substances have. Things which have weight exert pressure, and it is owing to the differences of pressure that disturbances take place in the atmosphere. These differences are brought about chiefly by *differences in temperature* and, to a smaller extent, by the amount of water-vapour present in the air. The source of heat is the sun. The radiant energy from the sun is termed insolation.

The Heating of the Atmosphere and its Effects.

The surface of the earth is warmed by insolation,

When air is heated it expands, and becomes less dense and lighter, bulk for bulk, than it was when cold. It therefore has less weight, and consequently exerts less pressure. Now it is a general rule that air flows from a region of *high* pressure to a region of *low* pressure. Thus colder, denser, and heavier air flows to a region where there is warmer, less dense, and lighter air, and gradually *forces the warm air to rise.* Thus there is a movement or circulation of the air. The air from colder regions moves along horizontally, forming *winds* on the earth's surface, while the rising air, moving vertically, is not felt as wind along the earth's surface, and a *calm* is the result.

In the case of our earth, the region of greatest heat, and therefore lowest pressure, lies round about

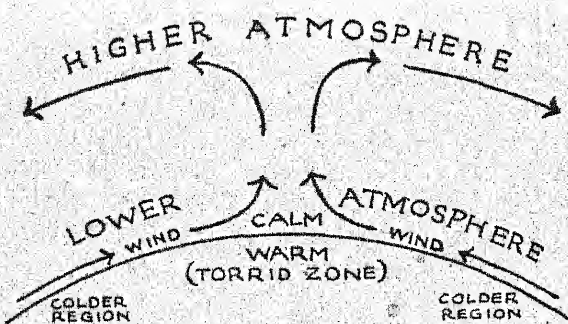
while the layers of air in contact with the earth are warmed by conduction. Surface air is then carried up by convection & in turn warms other layers by mixture & conduction.

In addition it [illegible]
radiation is directly absorbed by the more humid
portions of the atmosphere. Clear dry air is warmed
very little by insolation.

the Equator. The centre of this belt varies with the seasons, but, generally speaking, there is always a region round about the Equator where the air is being forced to rise. This upward movement of the air results in a region of calms at the surface of the earth, called the belt of low-pressure calms.

The Doldrums.

Sailors soon discovered where regions of calms lay. Sometimes their vessels lay becalmed in the



WARM AIR IS FORCED TO RISE.

belt that stretches between 10° N. and 10° S. of the Equator. They found that the weather there was hot and muggy, and rain fell almost continuously. There was practically no wind, but they soon learned to be on the look-out for violent and sudden thunderstorms and gales, which passed as quickly as they arose. The general condition of the weather produced a feeling of lassitude and dullness, and they called this part of the ocean the *Doldrums*, that is, the "dull" region.

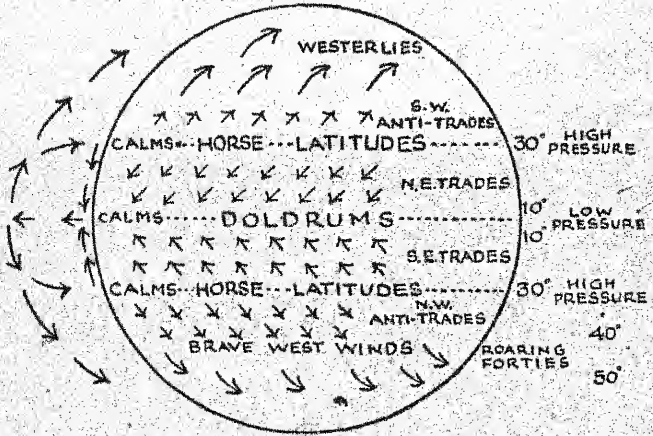
The Horse Latitudes.

Warm air rises from the Doldrums into the higher atmosphere. It flows northwards and southwards, gradually cools and becomes heavier, and then begins to settle down again. By the time it approaches and flows over latitudes 30° N. and 30° S. of the Equator, part of this heavy air descends to the earth's surface, and this gives rise to a belt of high-pressure calms. The weather is clear, and there is little or no rain, because of the descending air currents. Local winds may spring up, but they are light and variable. Ships lie becalmed in these regions, which sailors call the "Horse Latitudes." In days gone by it happened that ships bearing cargoes of horses were held up in these regions, and, owing to lack of water, very often part of this cargo had to be thrown overboard.

Winds over the Earth's Surface.

From this diagram it is readily seen that the air moves northwards and southwards from the high-pressure belts and produces winds. The early traders found that these winds blew regularly and steadily, and they called them the "Trade" winds. If the earth were at rest the Trade winds would blow directly north and south, but, because of the earth's rotation, they blow north-easterly in the northern hemisphere, and south-easterly in the southern hemisphere. Winds blowing in the opposite direction to the Trades are called the Anti-trades. If the earth's surface were completely covered with water the winds would blow regularly and without

interruption. But there are land masses (the continents) which are heated more quickly and cool more quickly than the ocean, thus forming regions of high and low pressure apart from the low- and high-pressure belts. This affects the winds, more especially in the northern hemisphere. In the southern hemisphere, however, there is a long sweep of ocean between the 40th and 50th parallels of latitude, and



CIRCULATION OF THE ATMOSPHERE.

here the course of the wind is uninterrupted. It blows from the west, gathering force as it goes, and is called by mariners the "Brave West Wind." The regions lying between 40° and 50° S. are called the "Roaring Forties," and the weather here is breezy, tempestuous, and bracing.

Winds and Weather.

From what we have said it is evident that the circulation of the atmosphere accounts for the differ-

ences in weather in different regions of the globe, apart from the latitude of the place concerned.

We must also bear in mind that the evaporation and condensation of water-vapour affects both temperature and pressure. Water-vapour is lighter than air. Moist air is lighter than dry air, bulk for bulk, because it contains water-vapour. Thus a region of moist air is a region of comparatively low pressure, and following the law we have already discussed, winds will spring up in it. The moist air is forced to rise and, as we shall learn presently, clouds form, rain falls, and perhaps a storm with thunder and lightning will be experienced. Thus the weather is affected by the amount of moisture in the air, but the chief cause of the variableness of the weather is the circulation of the atmosphere.

1) Explain why diurnal temp. changes are slight in cloudy weather. Do frosts occur in cloudy nights?
2. Explain why diurnal temperature changes are greatest over land.
3. What do you understand by Marine Climate & Continental climate?
4. The specific heat of water is about five times that of dry soil. How would this affect the temp. over land areas & also over water areas? What effect would the latent heat of vapourization have on them?
5) How is the air heated? How is it cooled?
6. What is insolation? Explain inversion of temperature.
Explain the process of radiation convection & conduction which take place in the atmosphere.

1. Define climatology, meteorology.
2. "Water surfaces reflect about 40% of the insolation that reaches them. What effect wd. this have on the temp of the water areas as compared with those of land areas.

CHAPTER II

METHODICAL OBSERVATION AND METEOROLOGY

Introductory.

If we wish to study the weather we must learn to observe and take notes.

We must first of all learn to observe methodically and correctly, and I am going to tell of some little experiments which will yield both pleasure and profit to those who care to carry them out.

The word "experiment" may conjure up visions in the reader's mind of apparatus such as is found in the science laboratory. Now this is a mistake, for our laboratory is the great "out-of-doors," and most of the apparatus we need can easily be made out of very ordinary materials.

The experiments I propose to describe will teach us to be *methodical*, and help us in time to form a habit of mind that may prove a great asset in our daily lives, by teaching us how to note, record, and recognize with accuracy and discrimination.

Meteorology.

Def. Meteorology is the science of the atmosphere. The name is derived from the Greek word *meteora*, which means "the air." It includes a study of the atmosphere and its phenomena. It deals with the commonplace and daily conditions of the weather x

as experienced at the surface of the earth, but it also deals with the less familiar conditions of the higher atmosphere.

The Higher Atmosphere and Aeronautics.

The higher regions of the atmosphere have been studied of late years more than ever before, especially since the introduction of aeroplanes and airships, the navigation of which demands a study of the air at both low and high altitudes.

There is still much to learn about the higher regions of the atmosphere and the conditions which prevail there. But for many years the study of the lower atmosphere has been methodically carried on. The Royal Meteorological Society of London has done much to encourage the study of the weather, and the Meteorological Office in London has collected a vast amount of information in regard to it. Public institutions and private individuals have made observations and kept records for years, so that we have an extensive knowledge of the atmosphere, especially the lower atmosphere.

A Practical Application.

It is being recognized more and more that a knowledge of the weather conditions is of great practical value for many purposes. Manufacturing, agricultural, plantation, and other work often depends to a great extent on the atmospheric conditions. Navigation at sea is helped or hindered by the weather, and it is obvious that as full a knowledge as possible of the atmosphere is essential for aeronautics.

Q. What practical importance is the study of meteorology? of climatology.

When air is compressed work is done on it & its temperature raised when it expands it does work & it is cooled. What effect wd this produce on the temperatures of the lower & higher layers of the atmosphere? Is this an important factor in the raising & lowering of temperatures?

CHAPTER III

LOOKING AT THINGS

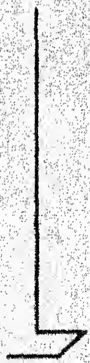
In this book you are going to learn how to look at things and take note of them. You will need a little practice to begin with, so I am going to show how you can use a shadow to teach yourself to **observe**.

This will give you practice in measuring and writing down your measurements. You will learn by doing and seeing for yourself. When you have written down what you have seen you can talk about it and be quite certain of what you are saying.

The Length of a Shadow and its Trace.

First of all I want you to measure the length of a shadow very carefully. The method of procedure is as follows:

Take a straight piece of wire and bend it to form a foot to stand upon. Set it up in a space in your garden which is open to the sun. Then brush a smooth, clear space about 2 feet all around the bottom of the wire.



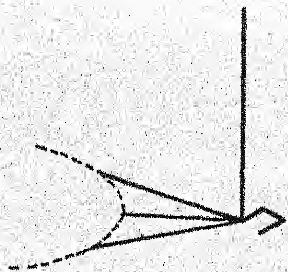
WIRE BENT TO FORM A FOOT TO STAND UPON.

Choose a day when the sun is shining brightly, and start your experiment some time about eleven o'clock in the morning. If it is "summer time"

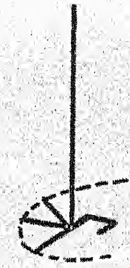
you should start an hour later by the clock. When all is ready, make a dot with some sharp point at the very tip of the shadow on the ground. Then draw a line along the shadow to the bottom of the wire. Measure the line in centimetres and millimetres. You can do this every half-hour, or every quarter-hour, just as you please.

Of course you need not stand by all the time. You can go away, and come back again when the next dot is due to be made.

As the half-hours pass, the lines you have drawn



WINTER SHADOWS AND TRACE.



SUMMER SHADOWS AND TRACE.

will be like the spokes of a wheel, but there will be a difference. This difference is the important thing. You should continue marking the dots and drawing the lines until two or three o'clock in the afternoon. When you have finished, draw *one curved line through the dots.* This curved line is what we shall call the **trace** of the shadow.

The Trace of a Shadow Varies.

You will notice that the position of the trace in relation to the wire varies according to the season

of the year. At first one might suppose that the trace would always be like a bow round the foot of the wire. But if you make three traces, one about midsummer, one about midwinter, and one half-way between these dates, you will find that in winter the trace as a whole bends *away from* the wire, and the oval curve points in the same direction, while in summer the trace as a whole bends *towards* the wire, and the oval curve lies about its foot. Notice that in both cases the shortest shadow is **at noon**. This is true of all shadows, no matter whether the shadow be that of a little pin, or of St. Paul's Cathedral.

Towards the equinoxes—that is, about March 21 and September 23—the trace will become a straight line. Think this out.

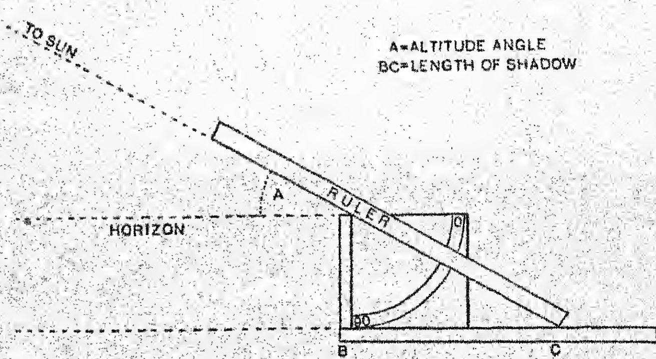
The Altitude of the Sun and a Home-made Measurer of Altitude.

Now there is one other thing I want you to do. You have noticed the variation in the altitude of the sun. Have you ever tried to measure the sun's height above the horizon?

To do this make the following simple piece of apparatus yourself. Take two pieces of wood, the longer piece about 46 centimetres in length, and the shorter about 16. Each should be about 6 centimetres wide and 1 centimetre in thickness. Make the shorter piece like a wedge, and then nail the two pieces together at right angles. Take a piece of stiff cardboard and mark a quadrant, or quarter of a circle, on it with a compass, as shown in the diagram, with the 0° uppermost, and whole degrees up to 90°. Then tack the piece of cardboard to the wood.

To find the altitude you must place the apparatus level, with the upright piece towards the sun. Move the horizontal piece round, keeping the upright piece steady as a pivot. Keep moving the horizontal piece until the top of the shadow coincides with the width of the board.

All that is now required to be done is to place a



HOME-MADE APPARATUS FOR FINDING ALTITUDE OF SUN.

ruler with one end on the top of the shadow, and let it rest on the top of the upright piece. The lower edge of the ruler will mark the altitude of the sun in degrees on the scale.

Warning.

Never on any occasion try to look at the sun with the naked eye. You will be blinded if you do. Always use a piece of smoked glass. It is unnecessary to look at the sun at all during this experiment, but I have seen people trying to do so.

Keeping a Record.

Now comes a *very important* piece of work. It is of no use your performing an experiment unless you keep a note of what you do and what you see. In other words, you must **keep a record** of your experiment, giving particulars of the date, place, and hour.

Drawing a Graph.

There is another thing you should learn how to do which is really quite easy, although some people think it is so difficult that only mathematicians can attempt it. We cannot all draw pictures, but we can make a simple kind of picture called a **graph.**

You will need a sheet of squared paper and a record of your experiment. It might be ruled out as follows:

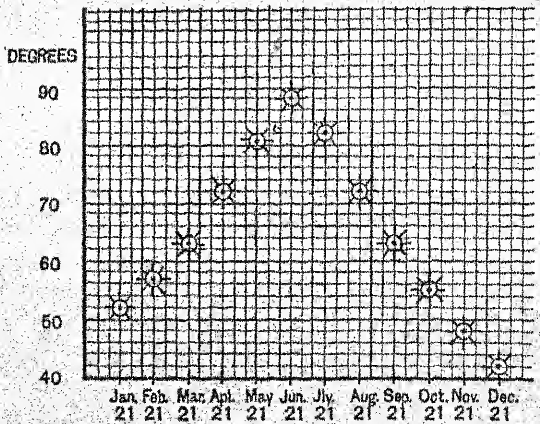
ALTITUDE OF SUN DURING 1918.			
January 21st	52°	July 21st	82°
February 21st ...	57°	August 21st	72°
March 21st	63°	September 21st ...	63°
April 21st	72°	October 21st	55°
May 21st	81°	November 21st ...	48°
June 21st	88°	December 21st ...	42°

Now these altitudes were taken at a place in India just outside the tropics, and from the graph you can see how high the sun got in the sky.

It will be interesting to compare your graph with the graph given here. This work was done by young lads who were very keen to find out all they could about the weather, because some of them hoped to get a chance of joining the Royal Air Force.

Conclusion to Preliminary Practice.

You now understand how to observe, to keep a record of your observations, and to express them



ALTITUDE OF THE SUN AT KALIMPONG, 1918.

graphically. This is splendid training, and you should continue it as you have opportunity, and as you pass to the very interesting task of weather study.

CHAPTER IV

HEAT AND THE ATMOSPHERE

Hot or Cold?

You will have noticed that the sun makes everybody and everything cast a shadow. But you may not have paid very much heed so far to the heat of the sun. All of us know that the sun is like a fire, and gives out **heat** as well as **light**. You will now learn about heat and hot days.

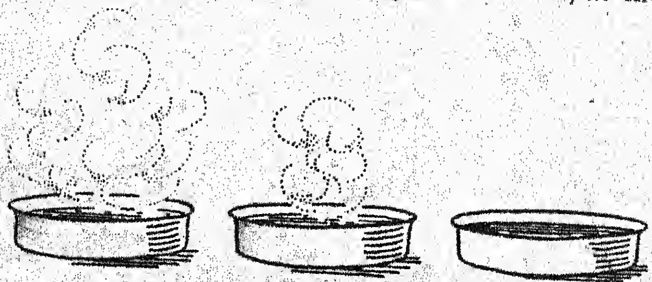
You must remember that all things can be heated and cooled. You can tell quite easily when a stone is hot. The air, too, can be heated and cooled; but it is not easy to tell with certainty when the air is hot or cold. You say that some days are warmer than others, but it would be hard to say *exactly* which was the hottest or coldest day by remembering how you felt. You cannot altogether trust your hands or your power of feeling.

An Experiment worth doing if you want a Surprise!

You will understand this better if you take three ordinary basins and place them in a row.

In the *right*-hand basin put enough *cold* water to cover the hand when placed in it. In the *centre* basin put about the same quantity of *tepid* water. In the *left*-hand basin put a similar quantity as *hot* as can be borne by the hand.

At the same instant put the right hand into the basin on the right, and the left hand into the basin on the left. Let the hands remain in the water until one feels thoroughly hot and the other thoroughly cold. Then very quickly plunge *both* hands, at the



Hot. Tepid. Cold.

A SURPRISE IN STORE FOR YOU.

same instant, into the tepid water Wait half a minute or so and notice what is felt.

Although the hands are in the same water, all of which is practically the same warmth, yet to the left hand it feels cold, while to the right hand it feels burning hot! What can be the matter?

Our Feelings are Untrustworthy.

After trying this experiment you will agree with me when I say that if we wish to find out whether a thing is really hot or cold we cannot trust our hands or what we feel. We cannot rely on ourselves to be quite sure about heat and cold. We need something upon which we can rely with certainty.

In the next chapter we shall discuss an *instrument* which is comparatively reliable in the matter of deciding when anything is hot or cold.

CHAPTER V

HEAT AND THE THERMOMETER

The Thermometer.

You will now discuss with me a little instrument which tells us about the warmth or coldness of the atmosphere. First of all its name is *thermometer*—that is, "a measurer of temperature."

You will notice that it consists of a narrow glass tube with a very fine **bore,** which is really a good deal finer than it looks. One end of the tube is sealed so that no air can enter. The other end is in the form of a **bulb.** Do you see the **quicksilver** or **mercury?**

The tube is **thickened** in many cases towards the front. This thickening of the glass acts as a *magnifying glass,* so that the tip of the thin column of mercury can be seen more readily. The tube is fixed to a stand on which **graduations** are marked. The little horizontal lines mark **degrees,** each line usually marking two degrees.

You notice the word *freezing.* This means that if you put the thermometer into water which is freezing, or ice that is melting, the mercury will sink to this point, called **freezing-point,** and marked 32°.

When the weather is very warm the mercury rises to perhaps 76°, and we call this **summer heat.** When it is just pleasantly warm we see that our

instrument shows that the temperature is about 60° or temperate.

Fahrenheit and Centigrade.

There are two kinds of thermometers. The one in common use is called the Fahrenheit thermometer, after the name of its inventor, Gabriel D. Fahrenheit. We have already mentioned its freezing-point, which is marked 32°. It also has a boiling-point—that is, the point at which water boils, or the temperature of steam—and this is marked 212°.

The other kind of thermometer is called the Centigrade thermometer. This is because there are 100 degrees, or "steps," between the freezing-point and the boiling-point. The name comes from the Latin words *centum*, "a hundred," and *gradus*, "a step." The freezing-point is marked 0°, and the boiling-point is marked 100°. This thermometer is used in laboratories and in science work generally.

Reading a Fahrenheit Thermometer.

Many people read a thermometer incorrectly. First of all it is necessary to stand some distance from the instrument. It should hang on a wall, and not be held in the hand. When reading it be sure *not to breathe* on it.

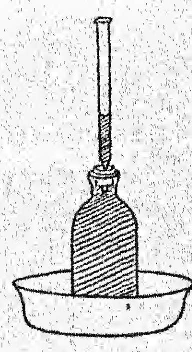
Then have your eye in line with the tip of the mercury. Do not look down at it or up at it. When your eye is level with the tip of the thread, glance to right and left, and notice the graduation nearest the tip. As a rule it is necessary to read only in whole degrees. Be careful to calculate the

correct reading, which gives you the **temperature** in degrees Fahrenheit.

Rise and Fall.

We speak of the "rise" and "fall" of the mercury. Do you know *why* the mercury rises and falls? Perhaps an experiment will illustrate this, and the experiment can be done at home.

Get an ordinary fairly large-sized bottle and fit a good cork to it. Then bore a hole in the cork and grease it. The hole must be a little narrower than the diameter of a piece of glass tube, which must be securely fastened into the cork, and sealed with wax or candle-grease. If you have not a tube the glass part of a **fountain-pen filler** will do.



A FOUNTAIN-PEN FILLER CAN SHOW EXPANSION.

Now fill the bottle quite full with water, coloured by adding to it a little black or red ink. Place the cork and tube in the neck of the bottle, and force it down until a little water rises in the tube above the cork. Seal in the cork, and tie a piece of white cotton round the tube at the level of the water. Then take a basin with a little cold water in the bottom, and gradually pour in hot water while the bottle is standing in the basin.

Watch carefully the *level* of the coloured water in the tube, and the piece of cotton. Is there a *fall* of the level or not? Take the bottle out of the basin and let it cool. What happens?

Do you now understand what rise and fall mean?

Obviously, heat made the water in the bottle take up more room or **expand,** and so it filled up more of the tube than it did at first. When the heat was taken away the water cooled and began to **contract**—that is, it took up less room than it did when it was hot.

We must bear in mind that, as a rule, **heat makes all things expand.** If the air in your room gets hotter, the mercury in your thermometer hanging on the wall gets heated by the air, and it expands. You will find a rise in the mercury when you have been in the room for a while, especially if you have shut the door and windows. Can you account for this?

Why Mercury is used for Thermometers.

Mercury is better than coloured water for thermometers. It can be easily seen: it readily expands and contracts. It does not stick to the tube, and at freezing-point it does not freeze. If the weather is very, very cold, it sinks below 32°. We then have so many **degrees of frost.**

Experiments demonstrate the Harmonious Working of Fixed Laws.

In the experiments we have done so far it is evident that there is a law governing what takes place. In the case of the shadow, we noticed that the shortest shadow was always at noon.* There is no variation of this law or rule, and it works day after day, as surely as the sun shines. There is

* "Noon" is not here 12:00 Greenwich Mean Time or any other kind of Mean Time.

harmony in the working of it, and the lengthening and shortening of the shadows are as regular and certain as the passing of the days.

Similarly, we see that heat makes all things expand, and when the heat is taken away the thing heated contracts to its original size. Here again is order and harmony.

A Notable Exception.

But there is a notable exception. In the case of water that is cooling, it is found that it contracts until a temperature of 4° Centigrade, or 39·2° Fahrenheit is reached. Then it gradually expands until 0° C. (32° F.), or freezing-point, is reached, when it turns into ice. This exception is of great importance. If the water went on contracting and becoming denser until it was ice, the ice would sink. In that case, when a pond or lake froze it would freeze from the bottom upwards. The mass of water would become solid ice. All fish and water-insects would be killed, and it would mean that almost all seas, lakes, and rivers, even in temperate regions, would hardly be water at all for any length of time, even in summer. The heat of the sun would not penetrate far enough to thaw the ice, and countries which now have mild climates would have much colder ones.

Why Water-Pipes Burst.

We have seen that water is most dense at 4° C., and that if it is cooled below that temperature it expands. When it reaches 0° C. it becomes solid and takes up more room than it did when it was a liquid. Suppose that a water-pipe is full of water.

In winter the temperature falls, and when 4° C. is reached the water begins to expand. The expansion continues until ice is formed, and the force of expansion is so great that very often the water-pipe bursts, and the burst is clogged by the solid ice.

When the thaw comes the ice turns into water and flows through the burst. It is not the thaw that has burst the pipe, as some people say, but the expansion of the water when it turned into ice.

CHAPTER VI

THE WIND AND A HOME-MADE WEATHER-VANE

" By at a gallop he goes, and then
By he comes back at the gallop again."

R. L. S.

Wind.

Who has not listened to the wind just as Stevenson did? Perhaps the imagery of a horseman at the gallop has never struck one, yet all of us at times have lain and listened to the wind on stormy nights.

What is the *wind?* Well, you remember the air that we spoke of when we were talking about heat. Now this air can move about. When it moves gently we scarcely notice it, but when it moves more quickly we feel what we call *wind.*

As the air moves over us it moves the branches of the trees, just as the water moves the branches of a tree that hangs down into a river. The moving air carries along with it very light things like dead leaves and dust, just as water would do.

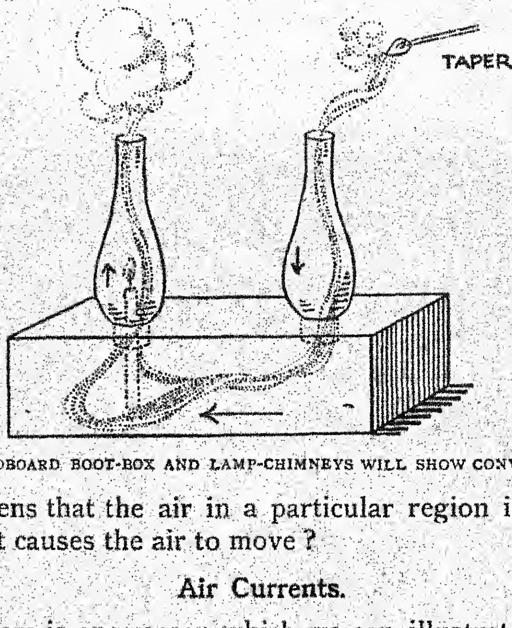
Take a long stick and wave it round your head. Move it slowly at first. What do you hear? Move it more and more quickly. What about the sound now?

So with the wind. When moving slowly it makes no sound, but when moving very fast it screeches in the trees as it pushes its way through the branches.

Wind shows its Presence by its Effects.

We cannot actually see the wind itself, because air is invisible. But we can see what it does. From what we see, and from what we know of the air, we all agree that when the *wind is blowing* the *air is moving*.

Wind, therefore, **is air in motion.** When the air is practically still there is no wind. But it rarely



A CARDBOARD BOOT-BOX AND LAMP-CHIMNEYS WILL SHOW CONVECTION.

happens that the air in a particular region is still. What causes the air to move?

Air Currents.

There is one reason which we can illustrate by a simple experiment, which anyone can easily perform. Take an ordinary cardboard box, say a boot-box without a lid, and two lamp-chimneys. Make two holes to fit the lamp-chimneys in the bottom of the

box. Light a piece of candle and place it inside one of the lamp-chimneys. In a little while you will feel hot air coming *up* the chimney. Fold up a strip of paper and make a taper. Light the taper and hold it above the other chimney. The smoke will be carried *down* the chimney. This shows that air is going downwards to take the place of the air which, after being heated, has risen upwards through the heated chimney. It is evident that it must be the moving air that carries the smoke downwards and then upwards. The experiment shows you what are called convection currents, and illustrates the great currents in the atmosphere which give rise to the Trade, Anti-trade, and other winds, which we discussed in the first chapter.

The Monsoons.

You saw in Chapter I. that the Trade-wind system would be universal if the earth were entirely covered with water. But the heating of the masses of land results in areas of low and high pressure being formed apart from the Doldrums and the Horse Latitudes. This upsets the Trade winds, and the chief example of this is the heating of the land mass of Asia. In summer land is hotter and in winter it is colder than the ocean. From what you already know it is evident that wind will blow from the sea to the land in summer, and from the land to the sea in winter. This happens in the case of South-East Asia and North Australia and other places, and gives rise to *seasonal winds* called Monsoons (from the Arabic *mausim* = season). The summer or wet monsoon blows from the south-west in India and

the south-east in China. In North Australia it is a dry south-east wind. The south-west monsoon in South-East Asia brings with it a vast amount of moisture. This warm wind is forced to rise to cooler altitudes when it encounters the coast and hills or mountains. Rain falls in great quantities, and the season (May to October) is called the "Rains." The winter or dry monsoon blows from the north-east in Asia. It is a dry wind because it blows over the land, and the season is warm (November to February) and hot (March to May). It blows partly over the Bay of Bengal, however, and brings a rainy season to part of Madras and Ceylon. At this time a wet monsoon blows towards Australia from the north-west. You will learn of other varieties of winds later on when we discuss weather charts.

How Wind is Named.

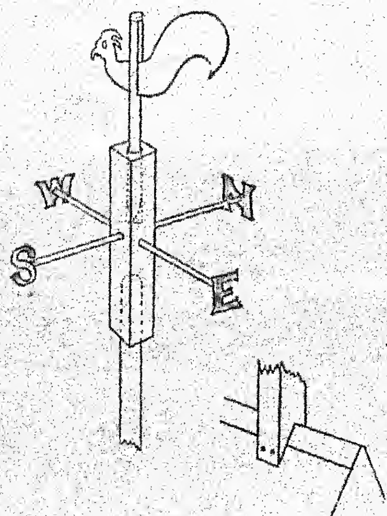
The wind is named after the *point* from which it blows. Thus, the north wind blows from the north. If you want to name a wind you must find the point from which it is blowing. This is not always easy. A straw does not help you very much, although it shows in a general way the direction of the wind. You need something that shows you clearly and without a doubt the point from which the wind is blowing.

A Home-made Weather-Vane.

Have you ever tried to make a "weather-cock" for your greenhouse or the top of the flagstaff in

your garden? It is easily made by anyone who is at all clever with his hands.

All you have to do is to get a piece of tin and hammer it out flat. Then with a sharp pair of scissors cut the tin into the shape of a cock, arrow, or any figure you choose. Some people prefer a racehorse or a man with a telescope. But, in any



A HOME-MADE WEATHER-VANE.

case, be sure that the tail half is larger than the head. Also cut out four fairly large letters—N, S, E, W. Then get a piece of a pole or a round rod of convenient size to hold the vane. Split or saw the rod far enough to allow you to slip in the vane. Then bind the top with wire. Point the other end of the rod to form a pivot. If you can tip it with metal or a nail it will swing better.

Then take a piece of a beam (3 or 4 inches thick) and bore a hole in one end, a little wider than the diameter of the rod. If your rod is tipped with metal drop a round piece of tin or a halfpenny or other small coin into the hole to form a bottom for the pivot to turn on. Bore two small holes for the cross rods, push them in and nail on the letters. If you intend to erect the vane on a pole, bore another hole for the pole as shown. It is a good plan to make a V-shaped cut in the wood for fastening to a roof. When all is ready polish the pointed part of the rod with grease, and put some oil into the hole to act as a lubricant. It is best to enamel or paint your home-made weather-vane. Then you can set it up, taking care that your N points to the north.

Prevailing Winds.

If you keep a record of the direction of the wind, you will probably find that there is one direction more frequently recorded than the others. Look around in your district for any group of trees or solitary trees on ridges or in exposed places. Notice if they point in any particular direction, or lean as a rule towards one side. See if this pointing or leaning is common to most of the trees or groups of trees. Find the general direction in which the branches of these trees point or lean, especially in exposed places like ridges and low hills. Compare this direction with the direction most frequently recorded in the wind record. From what you see you will be able to determine the direction of the

prevailing winds of the district with fair accuracy. The prevailing wind is the wind which blows most regularly all the year round.

Speed of the Wind.

An **anemometer** is an instrument for measuring the speed of the wind, and an **anemograph** records as well as measures the speed. This speed is calculated in miles per hour. A gentle breeze travels about ten miles, a strong breeze travels at anything between twenty and thirty miles per hour, a gale blows at a rate of between thirty and forty miles per hour, while a hurricane may reach a speed of seventy-five miles an hour, and often exceeds this rate.

Some Interesting Winds.

In different parts of the world there are local winds to which special names are given.

The **mistral** blows from the plateau regions of France and the Western Alps, and travels down the Rhone Valley towards the Mediterranean. The **föhn** blows in Switzerland, and is a warm, dry wind. The **solano** is the warm wind from Morocco and Northern Africa which blows across to Spain. The **sirocco** is felt in Italy, and is a hot wind carried from the desert regions of North Africa. The **bora** is a cold wind which blows from the Balkan Mountains towards the Adriatic. The **harmattan** blows towards the Gulf of Guinea from the parched Sahara, and is hot and dry. The **simoom** is the suffocating, burning wind that arises in the desert

regions of Africa, Syria and Arabia. The **chinook** descends from the Rocky Mountains, and sweeps across the prairies of North America. **Hurricanes** are common in the West Indies; **typhoons** occur in the China and other eastern seas, and **tornadoes** of great violence frequently pass over the central United States, and are known in tropical regions as well.

CHAPTER VII

CLOUDS AND ATMOSPHERIC DUST

A Little Cloud.

A simple little experiment will give us an idea of what a cloud really is better than anything else. Take an empty condensed milk tin. You know that when you open a condensed milk tin you bore two holes in the top. Why do you bore *two* holes?

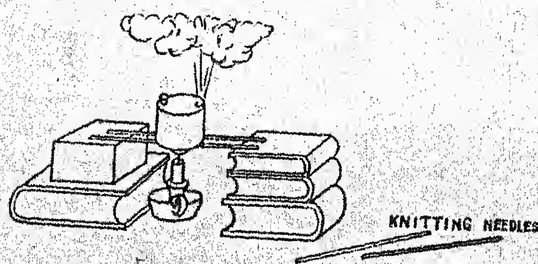
Well, take the tin and place it with one hole under the surface of some water in a basin. So long as one hole is out of the water the water runs in at the other quite easily, although the holes may be small. The smaller the holes the better for our experiment. When the tin is about a quarter full dry it and scrape off any paper that may be on the sides. Then set it up over a spirit-lamp or a candle, or place it on a fire, having first blocked up *one* of the holes with a piece of wood or a chip of cork, and proceed to boil the water. You will see a "cloud" of steam rising from the other hole.

Well, the big clouds above us are very much the same thing. In the case of your little cloud the heat of the candle or lamp changes the water into a substance in its form like air, which is called *vapour*. We cannot see the water for a while when it becomes vapour. Do you notice the *empty* space just below the cloud?

The vapour must be there, rushing out of the hole,

but we cannot see it. It is called **steam** when it is invisible.

As soon as the steam or vapour from the water rises a little and gets colder, we see it in the form of a little white cloud. Blow it with your breath. It can be blown away just as a big cloud in the sky is blown by the wind. What is it composed of? Hold a slate, a plate, or any *cold* thing over the cloud so that the cloud just touches it. At once the surface



USE WHATEVER IS AT HAND TO BOIL WATER.

of the slate is covered with **tiny drops of water.** This water must have come out of the tin in such minute drops that we did not see it as the water we know. We did not even recognize it as water when it was in the little cloud. But it was *visible*, and the tiny drops must have been bigger than those in the steam. Yet even these were so very minute that they floated, and were so light that they could easily be blown about in the air.

The Air is a Sponge.

When the air is dry it is in one respect somewhat like a sponge, and sucks up large quantities of water. You know that wind is air in motion, so

when the wind blows and the air is dry we get water "drying up." This, as well as water dried up by the sun, floats about in the atmosphere as vapour. You cannot see it. So long as it is in the form of vapour it is invisible. Under certain conditions of the atmosphere it becomes visible again and forms clouds.

The **clouds**, therefore, are made of minute drops of water. These drops are so very light and small that they float about in the air, and are blown about by the wind. They look white during the day and when the moon is shining, because the white light is reflected from them. At sunrise and sunset the clouds take the colour of the light in the sky, and appear pink, or yellow, or red, according to the rays of the setting or rising sun.

Atmospheric Dust.

The air, or atmosphere, contains countless numbers of minute grains of what is called atmospheric dust. This dust, or very fine powder, is the result of the wearing down of the matter on the surface of the earth, or of the very fine powdery nature of some things. It might be divided into **inorganic dust** and **organic dust.**

Inorganic atmospheric dust is the breaking down of dead matter, and there are numberless tiny particles of sand, iron, soot, wood, etc., floating about in the air, quite invisible under most circumstances. Organic dust is somewhat different. It may consist of the tiny pollen grains of plants, of spores, and of particles of decaying vegetable or animal matter. Living organisms also float about, known as micro-

organisms or microbes, and these, with the inorganic matter in the atmosphere, form what is known as atmospheric dust.

Water-vapour is present in the air in enormous quantities, and this is so light that, particle by particle, it does not possess enough weight to fall, and is carried about by currents of air. Now comes the *importance* of atmospheric dust. The tiny grains of solid matter in the atmosphere act as nuclei for the minute particles of water-vapour to *condense* on when condensation takes place in the atmosphere. This condensation occurs when warm, moist air rises into a region of cold air. The water-vapour becomes visible, being tiny globules of water with a speck of atmospheric dust as the centre. These are illuminated by the light, and when there are enough of them to be visible we see them as clouds.

Thus the minute dust particles in the atmosphere assist in the rapid formation of clouds, and, we shall see presently, in the formation of rain. Primarily, it is the condensation of the water-vapour that causes the tiny particles of water to be free in the air, and thus makes it possible for clouds to form.

CHAPTER VIII

HOW TO MAKE MODEL CLOUDS AND NAME CLOUD FORMATIONS

The sky owes a great part of its beauty to the forms which the clouds take. The white, billowy clouds which pile themselves in the heavens are majestic, and the long lines of low clouds are fascinating as they sail slowly across the face of the sky like great airships. The small, fleecy clouds, too, that float high up, take such wonderful formations that they compel us to look up and admire them.

Model Clouds.

It gives you a greater interest in the forms the clouds take if you can identify them and name them correctly. To do this you must become familiar with their general shapes, and I have found that an aid to learning the different forms is the making of rough models of the clouds in cotton-wool.

Cirrus Cloud.

If you take a little ordinary cotton-wool and pull it out with the fingers into very small and light fragments, you get an idea of the seemingly small clouds that form high up in the atmosphere. Arrange the pieces in regular or in sweeping lines, or in massed formation more or less regularly as you have seen the "feathery" clouds at sunset.

These clouds, called the **cirrus clouds,** are the highest of all. They form very high up in the air where the cold is intense, and are made up of very small particles of ice. When they stretch out in curves they are called the **mare's tail** or **lock of hair.** They form a glorious sight when they cover a clear blue sky and catch the rays of the rising or setting sun.

At night when these clouds form very thinly between us and the moon, haloes are formed. Other names for these haloes are *burrs* or *coronæ*, and they signify the approach of rain.

These clouds are also the cause of what are called *mock suns and moons.* These mock suns or moons appear as patches of bright light or rings, which are caused by the sunlight or moonlight passing through the ice crystals of which these cirrus clouds are formed.

Cumulus Cloud.

Take handfuls of cotton-wool and squeeze them in the hand to form lumps or masses. Make a heap as nearly as you can like the piles of white clouds you so often see towering above you. Very often these clouds are like steam escaping from a great engine. They seem piled on top of each other, and roll over one another. Sometimes they take the form of a "castle," and imaginative people see figures of men, animals, or other things in these woolly-looking clouds.

The **cumulus cloud** is not formed at so high an altitude as the cirrus cloud, and in India wonderful cloud effects on the Himalayas are often seen when

these clouds form at altitudes varying from 10,000 to 20,000 feet. The air currents between the mountains often cause the clouds to slide past each other, and one often sees one set of clouds travelling in one direction while quite near at hand another set is travelling in an entirely different direction.

Stratus Cloud.

To fix the idea of the **stratus cloud** in the mind, take some cotton-wool and roll it between the palms of the hands into long cigar-like pieces. Make several such pieces and stretch them out a little towards the ends. Try and copy these long narrow clouds you have seen near the horizon. Arrange them in a mass and see if they resemble the layers of cloud that often look like huge airships.

These clouds are called the **stratus** or "layer" cloud, and are the lowest of all. They never form much higher than 10,000 feet, and are often seen hovering along the hillsides and around the tops of mountains. They form in the early morning, usually before sunrise, over valleys, especially if the valley is a river valley or one containing a lake. When the sun gets higher in the sky these clouds usually disappear.

The Rain Cloud.

If you have ever watched, say during a fine early afternoon, the cumulus cloud drifting across the sky, you will have noticed, especially if the weather is hot and stuffy, that these clouds seem to collect and pile themselves up in one particular part of the sky. They spread out into large banks, one above

the other, with great rounded masses of white cloud uppermost. Very soon a formation known as **cumulo-stratus** (that is, a combination of cumulus and stratus) is seen, and the great **nimbus** or **rain** cloud rises in the sky like some great giant.

It begins to look threatening, and as it increases in size it shuts out the light, and it becomes dark and shadowy. Very often a breeze begins to blow, and before very long the rain begins to fall. Rain always accompanies the nimbus cloud, and when next you see a *rainstorm* approaching pick out the large masses of cumulus cloud and notice the great banks of stratus that also go to make up the cloud.

Fogs, Haze, and Mists.

When clouds form very low down near the surface of the earth, or just near the sea, we call them **fogs** or **haze**.

On cold hillsides we often find thin clouds formed. They seem to cling to the ground. These clouds are called **mists**.

There is no difference between the structure of **fogs, haze,** and **mists** and true clouds; the only difference is in the *altitude* at which they are formed. Condensation takes place when warm moist air is in the proximity of something which is colder. Fogs form over the sea, and on land fogs are frequently formed over damp and marshy places and in cool valleys, especially over a lake or river. In the early morning mists form round the hills, but as the sun gets higher these light clouds usually disappear.

In towns and cities there is in most cases a com-

paratively large number of little particles of soot and charcoal dust in the air. The soot and dust come in great part from the smoke which results from coal or other fires. When the air cools the water-vapour in it forms particles of water which collect round the particles of soot that are floating over the houses, and a low, thick cloud is formed. Over London and other big cities "pea-soup" fogs form. These are low, thick fogs containing a large proportion of soot particles (smoke) as well as particles of water. They almost blot out the sun-light, even at noon, and the small amount of light that filters through gives the fog a yellow colour. These fogs are very disagreeable and cause great inconvenience to travellers. Collisions are liable to occur, and every kind of traffic by air, sea, or land is greatly hindered by them.

CHAPTER IX

THUNDER AND LIGHTNING

A Thunderstorm.

LET us watch the approach of a thunderstorm. As we look we shall most likely see the rapid formation of great masses of cloud somewhere on the horizon. If it is hot and sultry there may be banks of cirro-stratus cloud higher in the sky, and as we look we shall see these roll up and ascend to form great quaintly shaped masses of cumulo-stratus or nimbus, the rain cloud. These great clouds become denser as the rain forms, and as there is a great uprush of air the result is a heavy shower of rain, or it may be of hail. Lightning may soon play in and out of the cloud, accompanied by the rolling of distant thunder. As the nimbus cloud spreads the sky becomes darker and the wind rises. Very often there is a sudden blinding flash, followed by a deafening crack of thunder. The rain begins to fall in torrents, flash after flash of lightning is seen, and the thunder booms steadily. The thunder re-echoes, and then seems to be dying away. By-and-by the sky clears, the rain stops, and the thunderstorm has passed over. There is a feeling of freshness, and the air seems clear.

Thunderstorms usually occur in hot or warm weather, when there are rapid ascents of warm air. These ascending air currents cause a great amount

of condensation, which results in large and dense masses of clouds. The thickness of the clouds prevents the sunlight from passing through them, and they look dark and threatening. As the clouds are carried upwards more condensation takes place, and raindrops form which may at first be carried still higher if the force of the ascending current is greater than the weight of the drops. If this happens they increase in size, and a point is reached when they fall because of their own weight. In falling they break up into smaller drops again. It often happens that the air at the higher altitudes is cold enough to freeze the raindrops. They then fall as hail. Thus hail often accompanies a thunderstorm.

Lightning.

Let us now consider what lightning is. We know that the clouds are composed of particles of water. When these clouds rise with the quickly rising air part of them forms raindrops. Some of these are of a greater size than the average raindrop, owing to their being added to when held in suspension by the force of the upward current. All are carried upward as a cloud. They are blown over and over each other and rub against each other in the uprush of air, and when the heavier drops of rain begin to descend because of their being heavier than the upward force, there is a breaking up into smaller drops, which fall as ordinary rain. Part of them may again be carried up and the process repeated so long as the warm uprush of air continues. The clouds in which this happens become charged with electricity.

From the cloud masses there is a discharge of electricity, perhaps between cloud masses containing different amounts of electricity or between the clouds and the earth. When the discharge takes place we see a **flash**. This flash is called **lightning**, and thus, in all probability, is a discharge of electricity in the sky. Great and fierce light accompanies such a discharge, which takes place instantaneously. It is visible practically as soon as the discharge takes place.

Thunder.

The very great heat produced by a flash of lightning causes the air through which it passes to expand very suddenly and very violently. It is just the same thing as happens when an explosion takes place.

You know that when an explosion takes place there is a loud **bang**. This bang or **clap** which we hear *after* we see the lightning is called **thunder**.

We hear it echoing between the clouds, or between the clouds and the earth, and it appears that there are many claps of thunder. It **rolls** as it echoes and re-echoes in the sky, or from hill to hill, and often sounds like a tremendous cannonade.

You have no doubt noticed that sometimes the lightning and thunder seem to be seen and heard simultaneously, while at other times a considerable period of time elapses between the flash and the clap. This is because light travels more quickly than sound, and we see it first and hear the thunder afterwards.

How to tell the Distance of a Thunderstorm.

Would you like to know how far off the next thunderstorm is when you see the lightning? All that you have to do is to **count the number of seconds** between the flash of lightning and the clap of thunder. You can tell how far off the thunderstorm is by counting **one mile** for every **five seconds**.

To count seconds say 101, 102, 103, etc. For example: I see the flash—101, 102, 103, 104, 105—I hear the clap. I have counted five seconds, therefore the thunderstorm is one mile away. Count 101, 102, 103, etc., *smartly*, and stop as soon as you hear the clap.

Sometimes you can just manage to say 101. Then the thunderstorm is very near. Perhaps you cannot even get your lips to form the numbers. Then the lightning flash took place perhaps just above you, or in any case very near at hand.

The Aurora Borealis.

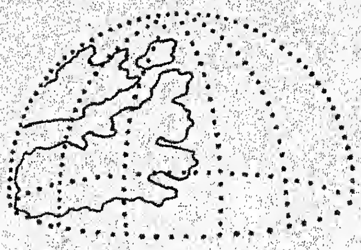
Have you ever seen the "Northern Lights"? Sometimes in the north are seen circles of light with long "streamers" or rays branching in all directions. The light is quivering, and gleams most beautifully. These lights are due to the electricity in the air in the Polar regions, where very few thunderstorms occur and there is little lightning. They seem to be electrical discharges, about which not very much is so far known.

CHAPTER X

"MACKEREL SKY" AND THE SEMI-SPHERE OF THE SKY

Semi-sphere of the Sky.

I WONDER how many of my readers have ever seen a "sea of clouds" from above? If you have never been up on a mountain and looked *down* on the clouds you have missed a wonderful sight. Below you is a stretch of clouds as far as the eye can see. As a rule, such a view shows the clouds to be of a fairly regular level and altitude. Above is the flawless blue of a cloudless sky.



THE SEMI-SPHERE OF THE SKY.

When you have had such a view you get an idea of the "**semi-sphere** of the sky," from the horizon right overhead to the horizon again. For keeping a *cloud record* it is usual to call the sky from horizon to horizon the **semi-sphere of the sky**, and imagine it to be divided into ten **divisions** or sections.

Each section can be considered as starting from the zenith, or point exactly overhead, and as being bounded by two lines which cut the horizon. The sketch gives you an idea of the arrangement.

According to the number of divisions containing clouds you can write down an approximate calculation in your record. Thus, in the figure showing the semi-sphere of the sky, you see that the greater portions of three divisions contain clouds. In your record you will enter "3" under the name of the kind of cloud. You will learn how to draw up a suitable table for your record when you come to the chapter dealing with a weather chart.

If there be no clouds, or practically none, we enter "o." If the sky be a drab grey, and completely covered with clouds, you put "overcast." If it is foggy or hazy you enter "fog" or "haze," as the case may be. If about half the sky be covered with clouds you enter "5" (*i.e.*, five sections out of ten) and so on. You must use your common sense, and your record should not only show the kind of clouds on a particular date, but should give a fair idea of the proportion of the sky that was covered with cloud at the time of recording.

"Mackerel" Sky.

You will most likely notice that on some occasions it is not easy to name exactly a certain cloud formation. In fact, you soon recognize that there are mixed formations of clouds.

A good example of this is what is known as "Mackerel Sky." You know what the back of a

mackerel is like. There are bands and dotted parts all scattered along the length of the back. In the mackerel sky the heavens are covered with a series of bands or lines of light cirrus clouds and small layers of cumulus. They appear spread more or less regularly right over the sky. We therefore name this formation **cirro-cumulus.** In a cloud record we always use contractions, and so cirro-cumulus would be written "ci.-cu.," and stratus is contracted into "str."

A Good Habit.

We know that habits come by constant repetition. Now it is as easy to form a good habit as it is to form a bad one. I believe it is a good habit, and one well worth forming, to make a point of looking up at and examining the sky every time we go out for a walk.

In spring, summer, autumn, and winter, the clouds and sky have a beauty all their own. Each season has its particular charm, and there is nothing that makes a walk or ramble out-of-doors more inspiring than to look up and consider the clouds, and to note all the surprises that nature has in store for us in field, hill, wood, and river.

For example, have you ever seen clouds going in opposite directions and passing each other? Can you explain this?

We must always bear in mind that clouds differ according to their altitude, and when a mass appears almost as one cloud it may really be two or more distinct masses at different altitudes.

Dwellers in town can look up at the sky even though their outlook on nature is narrower than in the country. I have seen many charming patches of sky from back alleys and courtyards, and have found that their glory is intensified by contrast with the squalor of the surroundings.

CHAPTER XI

RAIN AND THE RAINBOW

Rain.

THOSE of you who have never lived in a "dry and thirsty" land cannot fully appreciate what the word "rain" means. To those who have lived in a country in which the earth is parched and completely dried up for months at a time, the word "rain" recalls a joy and gladness unknown in regions which are more or less green all the year round.

In order to get an idea of what rain is and how it is formed, let us recall the experiment described in Chapter VII. Do you remember what happened when you placed a *little* cold slate near a *little* cloud? What do you think would happen if a *big* cold thing came near a *big* cloud?

Well, the very same thing happens as in the case of our little cloud and slate. The minute drops of water in the cloud join together and form bigger drops. Of course there is no big slate near, but a *big quantity of cold air* acts in the very same way. This happens high up in the air as a rule, and the newly formed drops fall to the earth when they are heavy enough to start falling.

In the first instance the tiny droplets of water from the condensation of the water-vapour in the air form clouds, and are so light that they remain suspended in the air and float about. Then, if they

are carried to still colder regions of the atmosphere more condensation takes place, and water is deposited on these small drops so that they increase in size and weight.

A Shower of Rain.

Rain, therefore, is water that falls from the clouds. It always falls in the form of beautiful drops which are called **raindrops**. Clouds usually appear before rain, but in some cases there seem to be hardly any clouds at all, and yet a fine rain is falling.

Have you ever *looked* at a shower of rain? As a rule, especially if you are out-of-doors, the chiet thing which has occupied your mind is to get shelter. Now there is a charm in falling raindrops, especially if it is a fine rain. The drops take on a silvery sheen as they dart downwards, and the whole landscape seems to shimmer. Trees, grass, flowers, and even the roads, fences and houses, appear "silvered" and glistening, and there is a general look of freshness. Colours of flowers are more brilliant. Stones and pebbles show their true markings or colourings, and rocks assume deeper and more pronounced shades. Leaves and grass are shining with a fresh greenness unseen when they are dry. The rain itself glistens, and when it stops raining the whole view is transformed by the dazzle of light upon water.

The Rainbow.

One ot the greatest transformation scenes in all the natural world is the formation of the glorious rainbow. There is hardly a human being, I should

say, who has not been fascinated at some time or other by the view of the "arc-en-ciel," or arch-in-the-sky, as the French call it.

If you have been standing with your back to the sun and looking towards the clouds from which rain is falling, you will have noticed that a **rainbow** is formed in the sky right opposite to where the

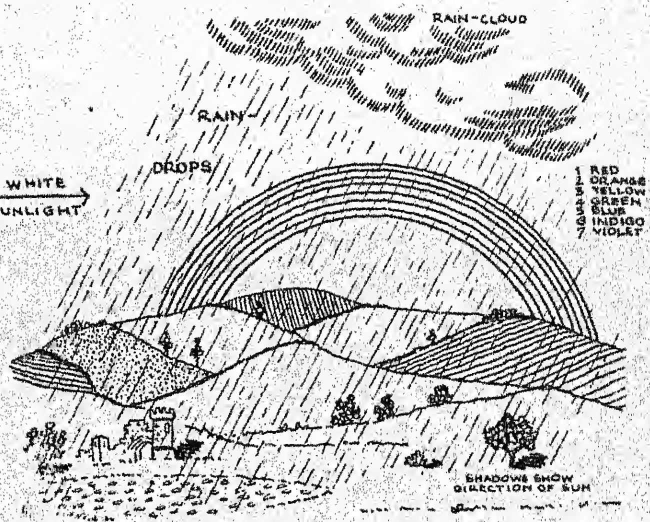


DIAGRAM TO HELP YOU TO REMEMBER WHAT HAPPENS WHEN A RAINBOW IS FORMED.

sun is. It seems to stretch right across the valley or fields, from horizon to horizon, or from field to field.

Is it any wonder that children should try to reach the rainbow and expect to find where the colours touch the ground, heedless of the fact that however far we go the rainbow still seems as far off as ever? In fact, it generally fades away before one has gone

very far. And why? Because the rainbow is made of **light**.

The diagram gives you an idea of what happens when there is a rainbow in the sky. You will see that the white sunlight is **broken up** into seven brilliant colours by the raindrops.

If we consider the raindrops in a shower, the colours are scattered in all directions—that is, in a circle round the rays of sunlight that enter the dispersing surfaces. We therefore see the coloured light in a circle because the reflecting and dispersing surfaces are in a circle. The amount of the arc we see depends upon the altitude of the sun and the distance we are situated above the horizon. If you see the rainbow from a high mountain or when up in an airship, it appears a complete circle if the sun is fairly low. The centre of the arc or circle is the point opposite where the observer is standing, and his situation must be between the sun and the shower, with the sunlight coming from behind him.

You should carefully examine the next rainbow you see. Note which of the colours is outermost and which innermost. See if you can pick out the red, orange, yellow, green, blue, indigo, and violet portions. Notice in which direction the shadows of the objects before you fall. Any drops of falling water will form a bow of coloured light when the sun is shining from behind the observer. You can see this at a waterfall or a big fountain. There is a waterfall in Switzerland, on the way to Andermatt, where a rainbow is seen whenever the sun shines into the valley.

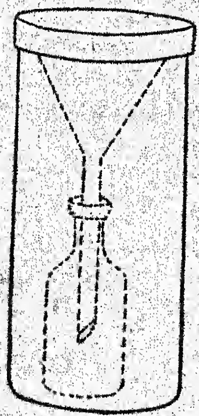
CHAPTER XII

THE MEASUREMENT OF RAINFALL AND THE RAINIEST PLACE IN THE WORLD

An interesting part of weather study is to collect and note the amount of rain which falls. To do this we require a rain gauge and a half-inch measure.

A Simple Rain Gauge.

You can make a simple form of rain gauge if you have a knowledge of soldering and cutting with tinman's shears. If not, it is a simple matter to get one made at the local plumber's or tinsmith's. You require a cylindrical can about 12 inches long and exactly 5 inches in diameter. A tin funnel must fit exactly into the mouth of the cylinder, and have a lip to cover the edge of the can and support the funnel. Any suitable bottle will do to collect the rain. The parts are fitted as shown here, and a fairly serviceable instrument results. If you paint or enamel your rain gauge it will not rust.

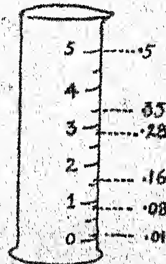


A HOME-MADE RAIN GAUGE.

The Half-inch Measure.

Besides the gauge it is necessary to have a half-inch measure. This is a glass cylinder, usually

with a lip, and is accurately graduated to hold half an inch of rain. It can be procured from the scientific instrument maker's or the optician's, and any dealer in glass apparatus could get one to order. A chemist might be able to get one for you from the firm who supply him with measuring-glasses.



A HALF-INCH MEASURE.

The top line is marked 5 or 50. This means that the measure holds 50 hundredths or one-half of an inch of rain when filled to this line. We usually say "point five." Similarly at 4 or 40 it reads "point four." Then there are ten smaller divisions between each of the longer lines. These give second decimal places. Thus, if the water rose to two small divisions above 4, the reading would be "point four two," which we would write down as 0·42 inches.

How to read the Level of Water in a Measuring-Glass.

Raise the measure *in line with* your eyes. Hold it at arm's length, straight in front of you. Then read the **lowest part of the curve.** Watch a chemist when he is making up medicine, and notice what he does when he reads his measure.

A Standard Rain Gauge.

The instrument usually used to collect rainfall differs in some of the details of construction from the simple one we have considered. The extra

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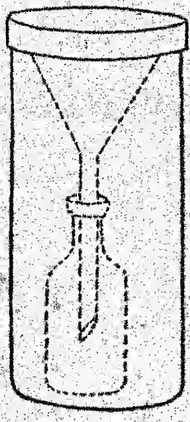

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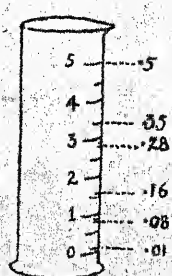

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A Standard Rain Gauge.

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parts are more or less precautions to guard against loss by evaporation or splashing. Sometimes a tin can with a handle is used instead of a bottle.

In all standard patterns the rim must be 12 inches above the ground, and have a diameter of 5 inches. There are several styles, such as the "Snowdon," "Symons'," and "Glaisher's."

The British Rainfall Organization.

The rainfall of the British Isles has been carefully noted for many years. As far back as 1860 Mr. G. J. Symons organized and founded what was called the British Rainfall Organization. In 1886 he printed a table of rainfall in Britain from 1776 to 1865. In 1861 he published a book entitled "British Rainfall," and it is still published every year. It contains the latest figures regarding rainfall in Britain. These figures are all carefully preserved, and the work of recording rainfall is carried on systematically under the Rainfall Organization.

How to Measure and Record the Rain.

We realize at once that it is impossible to collect all the rain which falls. Besides, it is quite unnecessary, as we shall see.

First of all, our gauge must be placed in an open space where the wind does not drive, and which is not overshadowed by buildings and trees. When placed thus with its rim 12 inches above the ground, the gauge is ready for collecting rain.

After the first shower some rain will be found inside the bottle. To measure this you must with-

draw the funnel and pour the contents of the bottle into the measure. Then read off the amount.

To record the amount you must draw up a table. The printed table shows rainfall for four successive days of twenty-four hours, and also the total up to date—that is, the amount recorded since the record started.

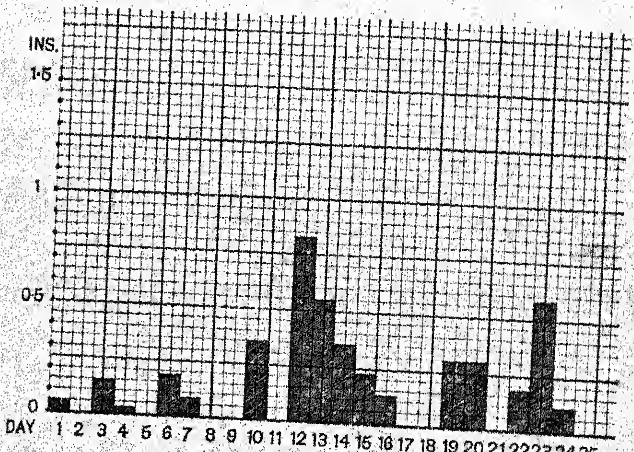
RAINFALL RECORD.		
DATE.	RAIN FOR DAY.	RAIN TO DATE.
June 15	0·25	16·44
June 16	Nil	16·44
June 17	1·46	17·90
June 18	0·68	18·58

An Inch of Rain.

We have been talking about inches of rain. Let us bear in mind that when we say we have had an inch of rain we mean that if none of the rain sank into the ground or ran away, and none evaporated, the area of surface under the shower would be covered to a depth of one inch. The rain gauge shows that this would be the case. As the rain falls fairly evenly over any area, we would get the same result at any point of the area under the shower.

Graphical Representation of Rainfall.

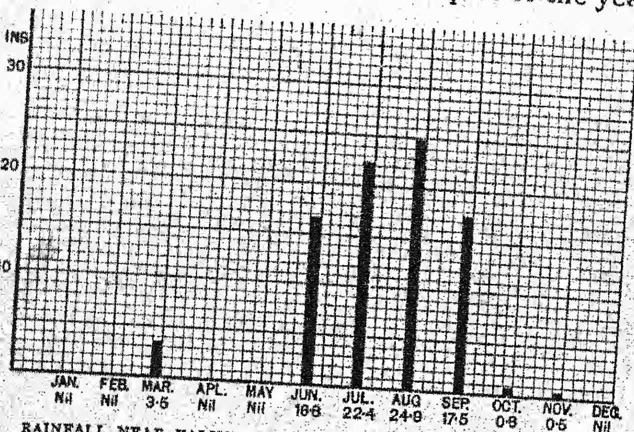
If you keep a record of rainfall you can make graphs that are concise, and tell at a glance the several amounts on different days. The diagram shows how rainfall can be recorded day by day during the month. A piece of squared paper, marked in tenths, can be used as shown, two small



DAILY RAINFALL CHART FOR NOVEMBER.

squares representing one-tenth inch of rainfall. The second decimal places must be drawn as accurately as possible. Thus, on the fourth there was a fall of 0·025 inches, on the twelfth there was 0·83, and on the twenty-third there was 0·58 inches. This chart is called a **Daily Rainfall Chart.** If you have records for all the months of the year, you can make a monthly rainfall chart. The printed monthly rainfall chart shown below is rather interesting. It

was compiled at a town called Kalimpong, which is situated in North-Eastern Bengal. You should compare it with your own monthly rainfall chart, and see how the two differ. You will be surprised to see the great amount of rain which fell during the months of June, July, August, and September. This is always the case in India, and the part of the year



RAINFALL NEAR KALIMPONG, BENGAL, FOR THE YEAR 1912.

between June 15 and September 15 is known as the rainy season, or simply as the rains. Notice that in December, January, and February there was no rain at all. This is the "cold weather," and, on the whole, the climate of India is delightful during these months.

The Wet Monsoon in India.

A region of low atmospheric pressure forms over the land mass of Tibet during May and the early part of June. Air begins to flow towards this region

from the region of higher pressure over the Indian Ocean. This warm wind blows over the sea, and becomes saturated with moisture. When it reaches the shores of India it is forced to rise over the hills and mountains, and in so doing gets chilled by expansion. This results in the formation of great masses of clouds, which herald the approach of the monsoon. The clouds are carried upwards with the air, and thunderstorms of great severity follow. Rain falls in very heavy showers, and continues to fall as long as the monsoon blows. The weather in June is very hot and close, but when the rain comes there is a welcome change. The heat is not so oppressive, the air clears, and there is water in abundance. Were it not for the monsoons India would be a desert. A failure of the monsoon, or even a deficiency in the precipitation, would mean famine in many districts, but irrigation has now done much to lessen the dangers of famine, especially in the Punjab.

The Rainiest Place in the World.

There is a range of hills in Assam, called the Khasi Hills, which gets the first of the south-west monsoon as it blows from the Indian Ocean up the full length of the Bay of Bengal. The hills lie in the direct path of the wind, and almost at right angles to it. The wind suddenly rises when it reaches them, and great precipitation takes place.

At a town called **Cherrapunji**, on the windward side of the hills, there is an *average* annual rainfall of 426 inches over a forty years' record of official figures. At some parts of the hills it is thought to

exceed this, and probably is nearer 500 inches than 400.

An Average of 518 Inches a Year.

There is a place called Waialeale, situated in one of the Hawaiian islands in the Pacific, which recently had an average annual rainfall of 518 inches during a period of four years. If this high average is kept up, Cherrapunji will have to take second place, and yield to Waialeale the title of "the rainiest place in the world."

CHAPTER XIII

FROZEN CLOUD AND FROZEN RAIN

Snow.

WE have noted that there is much beauty in a fall of rain. Is there not even more beauty in a fall of snow? If we examine the snowflakes minutely, we shall see that each individual flake is a perfect geometric pattern.

Before we do this, however, let us consider how snow is formed. If moist air is carried slowly upwards into a cold region of the atmosphere where the temperature is below freezing-point, and condensation takes place, the water-vapour is not condensed as tiny drops of water, but has time to crystallize as tiny particles of pure ice. These crystals are shaped like little needles or very thin small plates. They are all six-sided. They always form on each other or on the little plates at angles of 60°, and the result is a **snowflake.** Every snowflake has a six-sided appearance. Each is like a star or else like a regular hexagon, having six principal points or sides. All are alike in being **hexagonal**, although many have countless tiny points or edges, one and all being at an angle of 60° with its neighbour.

When a lot of snowflakes fall they form a shower of snow. Sometimes the wind blows the flakes about, and they collide with each other, or stick

fast to each other, and fall in little masses. It is then more difficult to distinguish their hexagonal nature, yet it is quite easy to catch single flakes. You should collect some flakes on a slate or on a black japanned tray, and examine them with a magnifying glass. You will be surprised at their beauty and symmetry.

Hail.

Now consider what is likely to happen if a quickly rising current of moist air encounters a layer or successive layers of air with a temperature below freezing-point. There will be sudden condensation, and crystallization will not take place. Instead, the drops of water will freeze into tiny balls of ice. The ascending current is usually of a cyclonic nature strong enough to carry these little balls to still greater altitudes. The chilling is so rapid that layer after layer of air is cooled below freezing-point, and layer after layer of ice forms round the original small pellets. In some cases, when the ascent is not so rapid, snow crystals form round the original pellets, and freeze hard, again to be covered with another layer of ice, if a sudden ascent occurs. Thus we get a **hailstone** consisting of layers of ice or snow frozen hard round a nucleus. Hailstones are generally about as big as fairly large shot, but sometimes they are as big as a hen's egg, weighing several pounds. When the hailstones become heavier than the force of the ascending currents of air, they fall suddenly.

Hail in Summer and Snow in Winter.

You have noticed that hail usually falls in summer, and snow in winter. In the case of winter the whole atmosphere, from the earth's surface upwards, is cold, often with a temperature below freezing-point. There are no sudden currents of warm rising air owing to the heating of the surface of the earth. Condensation takes place slowly, and snow is formed.

In summer it may happen, especially in very hot weather, that a current of air rises quickly, producing rapid expansion and consequent sudden cooling of the air, which causes rapid condensation. We have seen that this produces hail. Very rapid ascent and condensation takes place in the case of a thunderstorm, in which great masses of cloud form suddenly. Hence hail accompanies a thunderstorm, and thunderstorms usually happen in hot, sultry weather.

The rapid rising of air cannot happen when the air as a whole is cold or cool, and thus we get snow in winter, but as the atmosphere, especially near the earth's surface, gets greatly heated in summer, currents of air spring up and rise, in some cases very rapidly, and hail follows. This usually occurs in the warmer seasons of the year.

The conditions for causing a rapid rising of air are common in tropical lands, and hailstorms are often sudden and frequent at certain seasons of the year. Great damage is sometimes done to crops and animals in the fields. Whole countrysides are laid waste, and the leaves of trees torn to ribbons.

I once saw a field of cabbages over which a hail-storm had passed. The leaves were holed as if bullets had pierced them, and the whole crop was ruined.

Sleet.

Sometimes snow and rain fall together, or snow enters a warm layer of air and partially melts. In these circumstances we get what is called **sleet.** It is usually accompanied by wind, and we feel unpleasantly cold and wet, and the streets become slushy.

CHAPTER XIV

A HOME-MADE WEATHER CHART

Order and Method.

To be orderly and methodical does not always come by nature. Some people are rather inclined to be careless in little things, not very important in themselves; but this carelessness, if allowed to go on, may develop into a serious lack of that precision and orderliness which mean so much in modern business life.

You have learned a good deal about the weather now, and before you go any further it will be a good plan to see if you can arrange your knowledge in a concise and comprehensive form. You may not have kept separate records of temperature, wind, rain, etc., but you should now endeavour to draw up what is called a **weather chart**, and keep it going for a while until you are thoroughly familiar with your good friend the weather.

In order to do so, take a sheet of paper or an exercise-book and draw up a weather chart on the lines laid down here. You will then be commencing to study the weather in a methodical manner, and you will soon learn a great deal, because you will have to study for yourself. You will require no book to guide you if you have understood what has been discussed in the preceding chapters of this book.

A concise and collected study of the natural phenomena you see in the atmosphere each day will lead you to the interesting conclusion that there are **changes of weather** almost every day, and you will keep on the look-out for these changes.

A Daily Weather Chart.

It is advisable to draw up a daily weather chart to show the weather for every day of the month. You need not have a large number of columns; have just as many as you can record. Draw out the chart neatly in ink and pin it on a thin board, or paste it to a sheet of stout cardboard.

The following sample is a handy form in which to keep up your acquaintance with the weather and your interest in natural phenomena. Remember that only *careful* practice makes perfect, and slipshod ways of doing things make you careless and you grow indifferent. You keep up an acquaintance with anyone in whom you are interested, don't you? It is not a mechanical interest nor an irksome acquaintanceship if you feel it a pleasure, and profit by it in living a fuller life.

This is how we should study the weather. To take notes, keep records and draw graphs is good so far as it goes, because it educates us. But if we see no wonder or grandeur in the natural phenomena around us, we are becoming merely accurate machines.

DAILY WEATHER CHART.

FOR THE MONTH OF .... 19......

KEPT AT ....

DAY.	TEMP. AT 9 A.M.	RAIN FOR DAY.	RAIN TO DATE.	WIND.	CLOUDS.	REMARKS ON WEATHER.	CLERK.
1st	56°	1·36	6·82	S.W.	Cum.-str. / 8	Dull and overcast. Thunder and lightning.	C. R.
2nd	58°	0·02	6·84	S.	Cum. / 5	Clear intervals between showers. Rainbow.	C. R.
3rd	59°	Nil	6·84	S.E.	Cir. / 2	Fair weather. Sunny.	C. R.

Weather Study should be a Healthy Pursuit.

To study the weather you must go *outside* and see for yourself. This is healthy, and there is no end to the profitable pleasure that you can obtain if you go about it in the right way. But if you think merely of keeping a neat chart, or being able to talk about the scientific terms connected with weather study, you will soon become tired. You will cease to notice the *changes of the weather*, and you will forget

that were it not for these changes daily life would be a very different thing from what it is.

If all the days were exactly alike they would become monotonous. If they were always fine, sunny, and dry we would soon long for a refreshing shower of rain, a thunderstorm to clear the air, or a cooling breeze.

Weather study ceases to be book-work when we and the weather are acquaintances. We shall never lack company out-of-doors or in the open country if we have the clouds, the sky, the sunshine, the rain, the rainbow, and the wind as our companions.

CHAPTER XV

SOME INTERESTING METEOROLOGICAL INSTRUMENTS AND A BIG DIFFERENCE

WEATHER study becomes more and more interesting as one goes on. You will find that before very long you will be taking note of the weather and of the things which happen in the atmosphere as naturally as you look at the clock to see the time.

You will have gained by now, I hope, a *first-hand* knowledge of the weather. This knowledge will give you a fuller understanding of what is meant by **climate.** Climate is very important. It affects the nature, products, trade, industry, and population of a land and the part it plays in the life of the world.

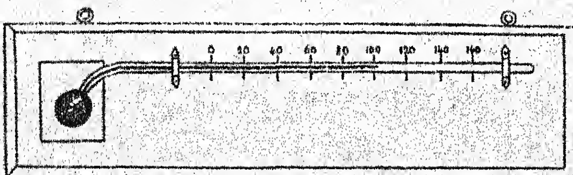
The Maximum and Minimum Thermometers.

In order to follow up the study of the weather you will require to know something of the more common instruments used in a conventional study of meteorology.

There are two special thermometers used for measuring temperature. Both are self-registering. One is called the **maximum thermometer,** because it registers the *highest* temperature reached during a given period of time. Examine the bore of the tube. Go along the tube until you come to the bend. Notice that the bore here becomes very narrow or

constricted. This constriction is the most important part of the instrument.

When the mercury in the bulb expands there is enough pressure from the volume of mercury in the bulb to force the liquid past the narrow or constricted part. Hence when the mercury is *expanding* it can pass into the tube, and the amount of expansion caused by the increase of temperature can be read from the top of the mercury column. When the increase of temperature ceases—that is, when the **maximum temperature** is reached—the mercury



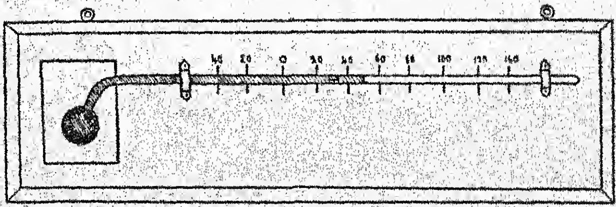
MAXIMUM THERMOMETER.

ceases to flow past the constriction. When the temperature begins to fall and contraction of the mercury takes place, the mercury already in the tube has not sufficient cohesion and surface tension to force it past the constriction. It therefore remains in the tube, and the end of the column farthest from the bulb marks the maximum temperature recorded.

After you have taken the reading you must "set" the instrument for the next reading. To do this you take the instrument in your hand with the bulb downwards. Give it a few vigorous shakes until you see the column of mercury join up right through the constriction and form one continuous column. There are several forms of this instrument, and any good style gives accurate readings.

Minimum Thermometer.

We also need to know the *lowest* temperature recorded. This is called the **minimum temperature**, and it is shown by the **minimum thermometer**. Examine the instrument. You will see that the tube is bent towards the bulb just as in the maximum thermometer. Examine the bore. It is the same width throughout. The liquid is alcohol. *Within* the liquid is a very small **index** or marker. The marker is so light that it is very easily moved by the expansion or contraction of the liquid.



MINIMUM THERMOMETER.

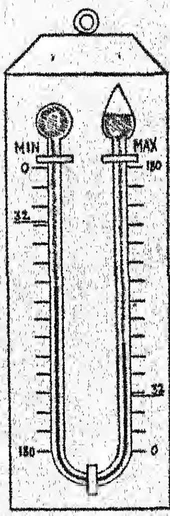
As the temperature falls the alcohol contracts. It carries the marker with it, and the marker remains *within* the liquid because the surface film of the alcohol resists being broken

When the lowest temperature is reached the alcohol stops contracting. As the index is still within it, the end of the marker farthest from the bulb marks the top of the column of alcohol when it was at its lowest contraction. When expansion takes place the alcohol flows past the marker, which is not carried along, as it is heavier than the alcohol. The minimum temperature recorded is the reading shown by the end of the index *farthest* from the bulb.

To "set" the instrument for the next reading hold it with the bulb uppermost until the index drops to the top of the alcohol column. It will be arrested by the surface film of the liquid, and will be drawn back again when the liquid contracts.

Six's Thermometer.

There is a combination of the maximum and minimum thermometers known as **Six's thermometer.** It registers the maximum and minimum temperatures simultaneously. It was first made in 1781 by an instrument-maker named Six, or Sixe.



SIX'S THERMOMETER.

The instrument consists of one long thermometer tube bent in the form of a U, and having a bulb at each end. The top of the fir-cone-shaped bulb contains slightly compressed air and alcohol vapour, and the upper part of the tube below the bulb contains liquid alcohol, which also fills part of the fir-cone-shaped bulb. In the alcohol in the tube is a small metal index. The bends of the tube contain mercury, which rises a little distance up both tubes. The remaining part of the tube and the round bulb are filled with alcohol, and the tube contains a metal index. The maximum tube is graduated from the bend upwards, and the minimum tube from the bulb downwards.

Expansion takes place towards the fir-cone-shaped

bulb, and the mercury pushes the metal index up the maximum tube until the maximum temperature is reached. The index clings to the sides of the tube, the lower end marking the maximum expansion. When contraction takes place the mercury pushes the other index towards the round-shaped bulb. When contraction ceases the index clings to the sides of the tube, and the *lower* end of it marks the minimum temperature. To set the instrument you must use a magnet to draw the metal markers down to the levels of the mercury after each reading.

The Daily Mean.

The daily mean temperature is obtained by adding the maximum and minimum readings and dividing by two. This is the recognized temperature to keep for making comparisons and keeping records.

After recording the maximum and minimum temperatures for a number of years, we can find what is called the **annual range of temperature.** The annual range of temperature is the number of degrees by which the average highest monthly temperature differs from the average lowest.

A Big Difference. Annual Range.

In some places the annual range is very great. At Yakutsk, in Siberia, there is a difference of over 100° between the average July temperature and the average January one. The average for July is about 65°, while the average for January is about −45°. Hence the difference is 65° minus − 45° or about 110°.

In some of the equatorial Pacific islands the average range is very small. This means that the temperature varies very little all the year round, there being sometimes only a few degrees of difference between the average summer and winter temperatures.

CHAPTER XVI

THE WEATHER-GLASS AND THE MOUNTAIN ANEROID

Climbing Mount Everest.

EVERYONE was interested in the Mount Everest Expedition. The gallant mountaineers set themselves a difficult task, and right manfully they performed it.

The party was equipped with a set of mountain aneroids for registering the height attained. The highest altitude reached in June, 1922, was 27,300 feet, which established a record in mountaineering. One of the climbers told me that one great difficulty they had to face was the lack of sleep. The air at high altitudes gets rarer as one ascends, and the deficiency of oxygen has bad effects on the human frame.

Now, the less air there is above us, the less weight it has to press downwards. Everything that possesses weight exerts pressure. When we speak of the **pressure of the atmosphere** we refer to its weight as a force which presses downwards towards the surface of the earth.

A Measurer of Atmospheric Pressure.

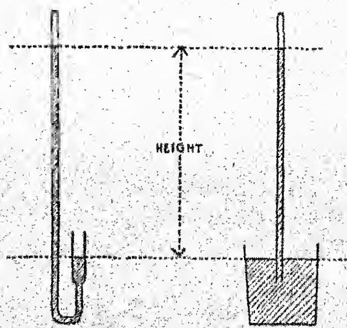
This can be illustrated by an interesting experiment for which you will require an empty barometer tube, some mercury, and a dish. Make a paper

funnel and carefully fill the tube with mercury to within an inch of the top. Place your finger on the open end of the tube and invert it. A big bubble of air will rise through the mercury column, and in passing will collect any smaller bubbles of air. Then invert the tube again and the big bubbles will ascend and pass out into the air. Very carefully fill the remaining inch, and use a pin to prick out any remaining bubbles. Place your finger on the end of the tube and invert it, holding the end of the tube and your finger under the surface of some mercury in a dish. Then take away your finger. The column of mercury will drop a little, and it will almost look as if air had entered the tube; but this is impossible. What has happened? You must think it out. First of all, bear in mind that the *air* is pressing downwards on the surface of the mercury in the dish. Then remember that because mercury is a liquid this pressure is exerted equally in all directions.

You will follow me when I say that now we have an instrument that will show us the pressure exerted by the atmosphere. It is evident that as the pressure increases it will support an increased column of mercury. Thus the height of the column will tell us something about the pressure of the air. We have therefore a **barometer**, or measurer of the weight of the air. This experiment is known as **Torricelli's experiment**, and it illustrates the principle on which all mercurial barometers are made. The space above the mercury is a vacuum, and is called the Torricellian vacuum.

Types of Barometers.

The two chief types of barometers are (1) the syphon pattern and (2) the cistern pattern. In the syphon pattern the tube is bent and attached to a stand, which is usually graduated. If the tube is fastened to the front of the stand the reading can be taken directly. A very common form has the tube at the back and a dial in front. The dial has

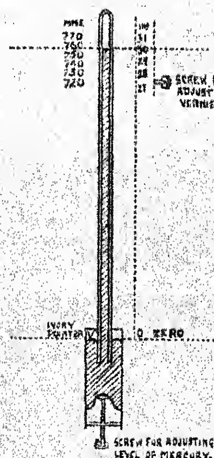


SYPHON PATTERN. CISTERN PATTERN.

a finger attached to a wheel over which passes a fine cord. To the cord glass weights are attached, one of which rests on the surface of the mercury. As the level rises the weight moves, and the cord moves the wheel and finger. The finger moves over the graduated dial, which has "Stormy," "Rain," "Change," "Fair," "Very Dry," or other words indicating the weather that may be expected. It does not follow, however, as we shall see later, that in *every* case the weather thus indicated actually occurs.

In the cistern pattern the tube is mounted on a stand which is graduated. A pointer slides beside the tube, and with its aid and the scale the height of the column can be measured. In the ordinary pattern difficulties in obtaining accurate readings arise, because corrections must be made for "capillarity and capacity."

Capillarity, it is worth noticing here, is an interesting phenomenon visible when narrow, "hair-like" tubes (Latin, *capillus*, a hair) open at each end are placed in a liquid. When the liquid wets the tube it rises in it; but if the liquid does not wet the tube (mercury, for instance) it falls inside the tube. Capillary attraction is very important in nature. Oil travels up a wick and sap up a tree by its agency.



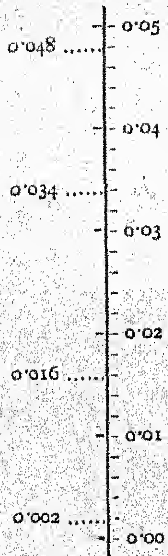
FORTIN'S TYPE OF CISTERN PATTERN.

Capillarity and capacity corrections are completely overcome and rendered unnecessary if **Fortin's barometer** is used.

This barometer has a collapsible cistern worked by a screw. By this means the level of the mercury in the cistern can be brought to the zero of the scale. The zero is marked by a little pointer made of ivory and visible through the glass cistern. The leather bottom is adjusted by a screw, and when the tip of the ivory pointer *just* touches its image in the mercury, the level and the zero are correct.

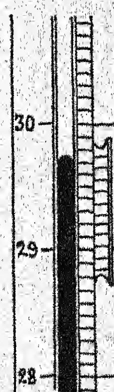
Reading a Vernier.

To get exact readings you will need to read the vernier or sliding scale. The vernier is adjusted by the screw at the side of the tube. It reads parts of the 0·05 divisions by dividing them into 0·002 divisions. The line shown in the diagram represents these subdivisions, which are sometimes marked 0, 1, 2, 3, 4, 5 on the vernier. Move the vernier until its zero is opposite to the tip of the mercury column. Then look along the graduation marks until you find a mark in the *sliding* scale in line with a mark on the *fixed* scale. Read the fixed scale first, and then add to it the reading of the vernier.



Thus, if the fixed scale reads 29·15, and the fourth small line of the vernier is in line with *any* line on the fixed scale, the reading will be 29·158. Some instruments show tenths, and the vernier reads hundredths. This is exact enough for most purposes.

The rule for reading the vernier is the same for all styles. This rule is: Look for a line on the vernier in line with a line on the fixed scale. The reading shown in the figure given here is 29·76 inches of mercury.



A "Weather"-Glass.

The barometer is sometimes called a "weather"-glass. We have already learned that the barometer registers the weight of the atmosphere according to its density, which is affected by heat. But the weight of the atmosphere is also affected by the amount of water-vapour that it contains. Air containing water-vapour is lighter, bulk for bulk, than air that is dry.

No air is *absolutely* dry, and it is obvious that the height of a barometer will be affected by the amount of water-vapour present in the air. We know from experience that dry air as a rule means dry weather, and damp air means wet weather; and so if the barometer is high we can expect dry and, therefore, fair weather, while if it is low we can expect wet and cloudy weather.

However, we know that in cyclonic and other disturbances winds bring rapid changes of weather locally, which are not always marked by the ordinary "weather-glass." But, though the pointing of the finger on the dial to "stormy," "fair," etc., may not always indicate the actual weather we are experiencing, yet we can be fairly certain that a rising barometer means settled and fair weather, while a falling one means the opposite.

One Inch for every 900 Feet above Sea-level.

If we took a mercurial barometer to the foot of a mountain, and if it were possible to climb the mountain, bearing the glass with us, we should find that for every 900 feet we ascended there would be a decrease of about one inch in the height of the

mercury column. The reason for this is clear, and we have in this fact a method of roughly determining the height of mountains and places above sea-level.

The Aneroid.

This is a barometer of a size and shape convenient for carrying about. It looks something like a watch. The chief part of the instrument is a flat metal box, circular in shape, which has little corrugations on the lid and sides. The sides are collapsible, and the box is finely made. It is partially exhausted of air, which gives it a spring-like motion when the pressure of the air varies. The lid rises and falls according to the pressure upon it. The movement of the top of the lid is communicated to a lever and fine spring, which transmit it to a finger which travels on a pivot in the centre of the dial. The finger turns over a carefully graduated dial on which heights of a mercurial column are shown in inches and decimals of an inch.

The Mountain Aneroid.

This is an aneroid with a dial specially graduated to show thousands of feet. Mountain aneroids are made to read between certain altitudes. The Mount Everest Expedition had three sets of instruments graduated to read from sea-level to 10,000 feet, from 10,000 feet to 20,000 feet, and from 20,000 feet to 30,000 feet.

Barographs.

Self-registering barometers are called **barographs.** They are made on the principle of the aneroid. The collapsible box causes movement which corresponds

to pressure. This is communicated to a lever, the thin end of which is in the form of a cup-like nib. The nib just touches the surface of a cylinder, over which a strip of paper is fastened. A drop of fine ink is put into the cavity of the nib, which records the variations on the roll of paper. Self-registering barometers are useful, but, like aneroids, require comparing and adjusting with a standard barometer from time to time. **No mercury** enters into the construction of aneroids and barographs.

How the air is cooled: (Read Smith's p. 4).
Inversion of temperature: " " " "

CHAPTER XVII

A TALK ON DEW, DEW POINT, AND FROST

Evaporation and condensation are going on continuously in the atmosphere. As a rule, this results in the formation of clouds, mists, or rain.

Under certain conditions of the atmosphere, however, a special form of condensation is met with, occurring at no great distance from the surface of the earth. Water is deposited from the atmosphere *and other things* in very tiny drops which are called **dewdrops**. This occurs at low elevations, and we may say that **dew** is the moisture deposited in small drops on cool surfaces from the air, from the ground, and from living plants. This water is deposited *at once.* No cloud or mist is necessary before the tiny drops of dew form. At one time it was thought that all the dew came from the air, but now it is recognized that some of the water comes from the ground, and in the case of dew on plants, the moisture is said to originate in the pores of the leaves.

Conditions Necessary for Dew Formation.

The day must be warm, with few clouds about, in order that full evaporation may go on. The following evening and night must be cool, with few clouds about, in order that condensation may take place. A clear sky is essential for dew formation. Clouds

check evaporation and condensation. The weather must be calm, or else the air will not be still long enough to allow of its contact with the ground, and thus permit of moisture being deposited. Wind will dry up any dew. Water must be present in some form on or near the earth's surface to supply the moisture to the layers of air that are next the surface.

Dew formation occurs at a comparatively short distance above the surface of the ground. Grass is commonly covered with dew when trees and taller shrubs are not.

Dew is not Counted as Rainfall.

The conditions for the formation of dew—viz., a warm day, a cool, calm night and a clear sky—are common in hot countries. In India great deposits of dew cover large tracts of the country. This deposit of moisture is not counted as rainfall.

Dew Point.

The temperature at which dew is deposited is called **dew point**. It is also known as the Critical Temperature. It can be determined by Daniell's hygrometer or the wet and dry bulb thermometer. Glaisher's tables give the dew point when the readings of the two bulbs are known.

Dew Ponds.

There are very interesting ponds or artificial reservoirs hollowed out in the ground to be found on the chalk Downs of the south of England. This part of the country is very dry, owing to the chalky nature

of the soil. The early peoples living in these regions made ponds with clay bottoms, and below the bottom was a layer of dry straw. This was a non-conductor of heat from the earth, and so a cool, clay surface was exposed to the atmosphere. During summer evenings dew was deposited and collected in the "dew ponds." This formed a water-supply for the otherwise waterless regions.

Hoar Frost or Rime.

We must remember that dew is sometimes formed when the temperature of the air is 32° F. or under. The night may be very cold, and then we find the dew deposited as **hoar frost.** You must not think that dew is first deposited as drops of water which freeze. This is not so. The dew is deposited *immediately as ice.* Thus hoar frost is composed of tiny crystals of ice deposited when the conditions of the atmosphere are favourable for the formation of dew but the temperature is 32° F. or under.

You may have noticed that the town is often free from hoar frost, while the fields in the surrounding country are not. This is because the smoke which gathers over the town does not give the clear atmosphere necessary for dew formation, and hence no hoar frost is formed.

A "Black" Frost.

When the conditions of the atmosphere are not favourable for dew, and it is very cold, we get an ordinary frost, sometimes called a **black frost.** No hoar frost or white frost is formed. Ordinary frost can only occur when the surface of the earth is at or

under freezing-point. A **frost**, therefore, is that condition of the air when water freezes. Any water on or near the surface of the earth freezes into ice. The ground becomes hard because the water it contains becomes ice. It is not until a *thaw* sets in that the ice melts, and the ground becomes soft by reason of the melting of the ice.

When the thermometer sinks below freezing-point, the number of degrees under 32° F. or 0° C. are called *degrees of frost*.

Temp.	Wt of a cubic foot of saturated vapour	Temp.	Wt
100 F.	19.766 grs.	-10 F	0.285
80	10.933	-20	0.166
60	5.744	-40	0.050
40	2.849		
20	1.235		
0	0.481		

CHAPTER XVIII

THE WET AND DRY BULB THERMOMETER. RELATIVE HUMIDITY BY TABLES

cf. Smith 14 ff

THERE is still another instrument used in weather study which calls for notice. It is called the **wet and dry bulb thermometer.** Before we can understand this instrument we must get an idea of *saturation.* We know that a dry sponge takes in water until a certain point is reached when it is full of water. It can hold no more, and if any more be poured upon it this water will fall from the sponge. The case of the air and the sponge differs with regard to their "porosity," but the idea of the air being "full of water" can be gathered from the illustration.

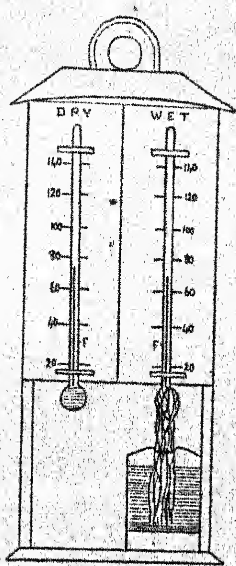
Saturation.

The air around us goes on taking in water-vapour until a certain point is reached when it can take in or hold no more. It is then said to be saturated or in a state of *saturation.* No air is absolutely dry. The degree of dampness is reckoned as a percentage. Fully saturated air is represented by 100.

The Wet and Dry Bulb Thermometer, or Mason's Hygrometer.

To get an idea of the *degree* to which the air is saturated we use an instrument called the Wet and Dry Bulb Thermometer. A common type of it is shown opposite. It consists of two exactly similar

thermometers mounted on a stand. One of the bulbs is free to the air. The other is surrounded by cotton threads which lead into a glass vessel below. Water rises up the threads and keeps them moist.



WET AND DRY BULB THERMOMETER.

The water on the threads in contact with the wet bulb evaporates slowly or quickly, according to the damp or dry state of the atmosphere. If the air be very dry, then evaporation goes on quickly. This evaporation produces a loss of heat, which lowers the temperature of the wet bulb. This is shown by a fall in the mercury column. If the air is moist, then evaporation is not so quick, and the loss of heat is not so great.

Evaporation ceases when the air is fully saturated. There is, therefore, no loss of heat, and the wet and dry bulbs show the same temperature. As a rule, however, there is a difference between the readings of the wet and dry bulbs. If the difference is great, then a considerable evaporation is going on, and the air is dry. If there is only a slight difference there is little evaporation and the air is moist.

Relative Humidity.

When we consider the humidity of the air we must take into account two things. The first is the

amount of water-vapour present in the air, and the second is the quantity of water-vapour required to saturate it fully. Taking this into consideration, there are methods by which relative humidity can be calculated. For our purpose it is unnecessary to go into these calculations. We shall use a wet and dry bulb thermometer and hygrometrical tables, and by so doing can read off the relative humidity at a glance.

How to Find Relative Humidity.

1. Be sure that the threads are moist, and that water is in the vessel.

2. Read the dry bulb and then the wet bulb, and note these readings down.

3. Look up the tables given here. Find the dry bulb reading corresponding to the one you have noted down, and then run down the wet bulb column until you come to your wet bulb reading as noted down. Opposite to this in the next column is the *relative humidity* shown as a percentage. The tables given here show a fairly wide range of readings, and are reproduced by permission. A full range of readings and other useful tables are given in a book entitled "Hygrometrical Tables," by James Glaisher, F.R.S.*

* This book is published by Messrs. Taylor and Francis, Red Lion Court, Fleet Street, London.

HYGROMETRICAL TABLES FOR USE WITH THE WET AND DRY BULB THERMOMETER

Dry.	Wet.	R. H.
38	38	100
	37	91
	36	83
	35	75
	34	68
	33	62
	32	56
	31	50
	30	45
	29	41
39	39	100
	38	92
	37	84
	36	77
	35	70
	34	63
	33	57
	32	52
	31	47
	30	42
40	40	100
	39	92
	38	84
	37	76
	36	69
	35	63
	34	57
	33	51
	32	46
	31	42
41	41	100
	40	92
	39	84
	38	77
	37	70
	36	64
	35	58
	34	53
	33	48
	32	43
42	42	100
	41	92
	40	85
	39	78
	38	72
	37	66
	36	60
	35	54
	34	49
	33	44
43	43	100
	42	92
	41	84
	40	78
	39	71
	38	65
	37	59
	36	54
	35	49
	34	45
44	44	100
	43	92
	42	84
	41	77
	40	71
	39	65
	38	59
	37	54
	36	49
	35	45
45	45	100
	44	92
	43	85
	42	78
	41	72
	40	66
	39	60
	38	55
	37	50
	36	46
	35	42
	34	38
46	46	100
	45	93
	44	86
	43	79
	42	73
	41	67
	40	61
	39	56
	38	51
	37	47
	36	43
	35	39
47	47	100
	46	93
	45	86
	44	79
	43	73
	42	67
	41	61
	40	56
	39	51
	38	47
	37	43
	36	39
48	48	100
	47	93
	46	86
	45	79
	44	73
	43	67
	42	62
	41	57
	40	52
	39	48
	38	44
	37	40
49	49	100
	48	93
	47	86
	46	79
	45	73
	44	67
	43	62
	42	57
	41	53
	40	49
	39	45
	38	41
	37	37
50	50	100
	49	93
	48	86
	47	80
	46	74
	45	68
	44	63
	43	58
	42	53
	41	49
	40	45
	39	41
	38	37
	37	34
51	51	100
	50	93
	49	86
	48	80
	47	74
	46	68
	45	63
	44	58
	43	54
	42	50
	41	46
	40	42
	39	38
	38	35
52	52	100
	51	93
	50	86
	49	80
	48	74
	47	69
	46	64
	45	59
	44	54
	43	50
	42	46
	41	42
	40	39
	39	36
	38	33
53	53	100
	52	93
	51	86
	50	80
	49	74
	48	69
	47	64
	46	59
	45	55
	44	51
	43	47
	42	43
	41	39
	40	36
	39	33
54	54	100
	53	93
	52	86
	51	80
	50	74
	49	69
	48	64
	47	59
	46	55
	45	51
	44	47
	43	43
	42	40
	41	37
	40	34
55	55	100
	54	93
	53	87
	52	81
	51	75
	50	70
	49	65
	48	60
	47	56
	46	52
	45	48
	44	44
	43	41
	42	38
	41	35
56	56	100
	55	93
	54	87
	53	81
	52	75
	51	70
	50	65
	49	60
	48	56
	47	52
	46	48
	45	44
	44	41
	43	38
	42	35
	41	32
57	57	100
	56	93
	55	87
	54	81
	53	75
	52	70
	51	65
	50	61
	49	57
	48	53
	47	49
	46	45
	45	42
	44	39
	43	36
	42	33
	41	30
58	58	100
	57	93
	56	87
	55	81

HYGROMETRICAL TABLES FOR USE WITH THE WET AND DRY BULB THERMOMETER

Dry.	Wet.	R. H.
58	54	76
	53	71
	52	66
	51	61
	50	57
	49	53
	48	49
	47	46
	46	43
	45	40
	44	37
	43	34
59	59	100
	58	94
	57	88
	56	82
	55	76
	54	71
	53	66
	52	61
	51	57
	50	53
	49	49
	48	46
	47	43
	46	40
	45	37
	44	34
60	60	100
	59	94
	58	88
	57	82
	56	76
	55	71
	54	66
	53	62
	52	58
	51	54
	50	50
	49	46
	48	43
	47	40
	46	37
	45	34

Dry.	Wet.	R. H.
61	61	100
	60	94
	59	88
	58	82
	57	77
	56	72
	55	67
	54	62
	53	58
	52	54
	51	50
	50	47
	49	44
	48	41
	47	38
	46	35
62	62	100
	61	94
	60	88
	59	82
	58	77
	57	72
	56	67
	55	62
	54	58
	53	54
	52	50
	51	47
	50	44
	49	41
	48	38
	47	35
63	63	100
	62	94
	61	88
	60	82
	59	77
	58	72
	57	67
	56	63
	55	59
	54	55
	53	51
	52	47

Dry.	Wet.	R. H.
63	51	44
	50	41
	49	38
	48	35
64	64	100
	63	94
	62	88
	61	82
	60	77
	59	72
	58	67
	57	63
	56	59
	55	55
	54	51
	53	48
	52	45
	51	42
	50	39
	49	36
65	65	100
	64	94
	63	88
	62	83
	61	78
	60	73
	59	68
	58	63
	57	59
	56	55
	55	51
	54	48
	53	45
	52	42
	51	39
	50	36
66	66	100
	65	94
	64	88
	63	83
	62	78
	61	73
	60	68

Dry.	Wet.	R. H.
66	59	64
	58	60
	57	56
	56	52
	55	48
	54	45
	53	42
	52	40
	51	37
67	67	100
	66	94
	65	88
	64	83
	63	78
	62	73
	61	68
	60	64
	59	60
	58	56
	57	52
	56	49
	55	46
	54	43
	53	40
	52	37
68	68	100
	67	94
	66	88
	65	83
	64	78
	63	73
	62	68
	61	64
	60	60
	59	56
	58	52
	57	49
	56	46
	55	43
	54	40
	53	37
69	69	100
	68	94

Dry.	Wet.	R. H.
69	67	88
	66	83
	65	78
	64	73
	63	68
	62	64
	61	60
	60	56
	59	53
	58	50
	57	47
	56	44
	55	41
	54	38
70	70	100
	69	94
	68	88
	67	83
	66	78
	65	73
	64	69
	63	65
	62	61
	61	57
	60	53
	59	50
	58	47
	57	44
	56	41
	55	38
71	71	100
	70	94
	69	88
	68	83
	67	78
	66	73
	65	69
	64	65
	63	61
	62	57
	61	53
	60	50
	59	47
	58	44

Dry.	Wet.	R. H.
71	57	41
	56	38
	55	36
72	72	100
	71	94
	70	89
	69	84
	68	79
	67	74
	66	69
	65	65
	64	61
	63	57
	62	54
	61	51
	60	48
73	73	100
	72	94
	71	89
	70	84
	69	79
	68	74
	67	70
	66	66
	65	62
	64	58
	63	54
	62	51
	61	48
74	74	100
	73	94
	72	89
	71	84
	70	79
	69	74
	68	70
	67	66
	66	62
	65	58
	64	55
	63	52
	62	48

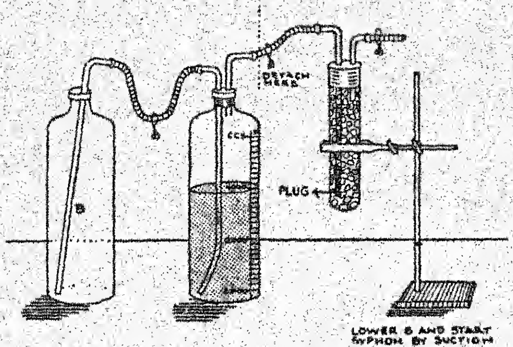
CHAPTER XIX

A CHEMICAL HYGROMETER. RELATIVE HUMIDITY BY CALCULATION

A Test in Accuracy.

If you are a student, or have access to a laboratory, get permission to make a chemical hygrometer, and calculate relative humidity. It is an interesting experiment, and will test your power of working accurately.

Set about it in this way. Fill a fairly large test tube with fused calcium chloride. Then get a cork



A CHEMICAL HYGROMETER.

to fit it. Fit glass and rubber tubes as shown. Plug the long tube *loosely* with cotton-wool to prevent little pieces of calcium chloride choking it. Then put it into the test tube and close the cork. Seal the cork and tubes with wax, and make the apparatus

airtight. Close both clips and weigh the tube. Take two large bottles as an aspirator, and attach one rubber tube of your test tube to the bottles as shown in the diagram. Then open your clips, and draw off a known number of cubic centimetres of water. This means that you draw into the aspirator a known volume of air. Stop the flow at the moment the quantity decided upon has been drawn off. Then close the clips and detach the tube. Weigh the tube again.

Relative Humidity by Calculation.

Then work as follows:

1. Note the temperature of the room.
2. From the given table find the *saturation humidity* for this temperature.
3. Calculate the number of grammes of water obtained from one litre of air, and get the *absolute humidity.*
4. Then divide the absolute humidity by the saturation humidity, and get the *relative humidity.*

Here is an example:

Temperature of room = 60° F.

Second weighing of test tube = 90·151 grammes.
First " " " = 90·142 "
∴ gain in weight = 0·009 "

In 2·5 litres of air the gain was 0·009 grammes.
In 1 litre " " " 0·009 ÷ 2·5
= ·0036 grammes.

$$\therefore \text{relative humidity} = \frac{\text{absolute humidity}}{\text{saturation humidity}} = \frac{0{\cdot}0036}{0{\cdot}0131}$$

= ·27 or 27 per cent.

The amount of air drawn through in this experiment was 2·5 litres.

The table given here is for use with a chemical hygrometer. I am indebted to Mr. Frank Spence, M.A., B.Sc., of Edinburgh, for the table and the term "saturation humidity."

Temperature in F°.	Weight of Aqueous Vapour in 1 Litre of Air.
	Milligrammes.
32°	4·8
40°	6·5
50°	9·3
60°	13·1
70°	18·3
80°	25·0
90°	33·9
100°	45·3
110°	59·8
120°	68·4

CHAPTER XX

A METEOROLOGICAL RECORD FOR ALL

WE have now gone into the scientific side of weather study in sufficient detail to enable us to draw up a fairly full **meteorological record.** The actual keeping of even a few records is in itself a valuable training if done in a business-like way. For our purpose, it is not so much the number of records that counts as the **method** in which they are taken. Punctuality in recording helps to form the habit of regular attention to duty, and we shall soon realize that we cannot take at any other time a reading that ought to be taken at a specified time. We must grasp our opportunities of recording, especially in the case of rare or unusual phenomena. Procrastination is fatal when we are dealing with such a variable thing as the daily weather. All readings should be faithfully and honestly recorded. If we are to receive the true *education* that is possible from a study of the weather we must work conscientiously, accurately, and with the desire to learn more, see more, and appreciate more of the wonderful natural phenomena with which we are brought face to face each day.

A sample meteorological record for general use is given opposite. We may not be able to keep all the records suggested, but we should keep as many as our apparatus will allow.

JUNE. DAILY METEOROLOGICAL RECORD. 19......

KEPT AT ....

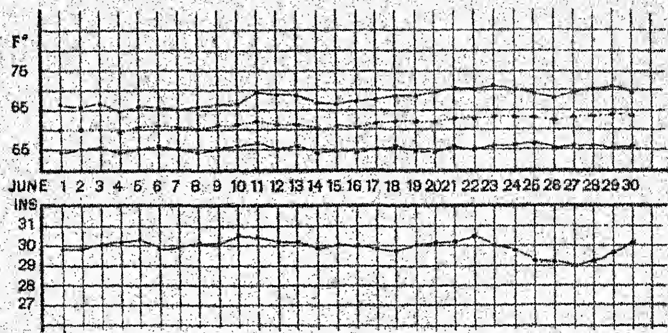
..................FEET ABOVE SEA-LEVEL.

DAY.	MAX.	MIN.	DAILY MEAN.	DRY.	WET.	REL. HUM.	BAR. PRESS.	RAIN FOR DAY.	RAIN TO DATE.	WIND.	CLOUDS.	REMARKS ON WEATHER.	CLERK.
1	67	58	62·5	60	54	66	29·54	0·26	3·42	S.W.	Cum. / 4	Clear and bright.	C. R.
2	66	59	62·5	59	55	76	29·52	1·34	4·76	W.	Cum.-str. / 6	Overcast Raining. Muggy.	C. R.
3	68	60	64	62	52	50	29·60	Nil	4·76	S.	Cir. / 3	Fair weather. Bright sunshine.	C. R.
4													

A Meteorological Station.

In schools and colleges it is a comparatively easy matter to establish a little meteorological station. I feel sure that those of you who have been truly interested in what a study of the daily weather teaches would be glad to collect such instruments as are available and place them on the wall of some shady verandah, porch, or lobby. We do not need to go to the expense of making a special place. For a beginning **make use of what you have,** be it only an ordinary Fahrenheit thermometer. You will find out about a "Stevenson Thermometer Screen" and other things as you go on.

MAXIMUM, MINIMUM, AND DAILY MEAN TEMPERATURES.



BAROMETRIC PRESSURE.

A Record Board.

All of us can possess a record board. An ordinary drawing-board or a stout sheet of cardboard will do.

It will form a centre of attraction if hung up in a prominent place, and will create an interest in the study of the daily weather.

On the previous page is a sample of how records might be graphed. All such records would be pinned on the record board.

1. What is meant by the mean daily temperature
2. How is the mean monthly temp. [illegible] obtained?
   (Cf. Smith p. 8)

CHAPTER XXI

WEATHER CHARTS AND WEATHER FORECASTS

Weather Reporting.

OUR study of the weather will be incomplete if we do not consider briefly some of the modern methods of recording weather on maps, and the inferences that are drawn from them. These maps are drawn from information collected each day by meteorological offices situated in various parts of the world. These offices are in touch with trained observers who are situated at various places on land and travel by ships at sea. The observers take readings simultaneously at fixed intervals, and send them by wireless or telegraph to the central office. All these reports are recorded and studied, and experts draw up what are called weather charts. The Meteorological Office in London supplies information which is published in the daily press. The information is comparatively easy to obtain because of the large number of ships travelling in the south-western, western, and northern seas, from which most of the weather changes come to Northern Europe. But it is more difficult in the case of Australia, where most of the weather changes come from the south. Few ships traverse the southern ocean, and thus the regions from whence observers can send reports are restricted.

Cyclones and Anticyclones.

Cyclones are winds which are really big swirls of air. They are very common in temperate latitudes, where the stronger, permanent winds are not so effectively felt, and also in monsoon areas when the seasonal winds are dying down and changing. They are caused by the formation of comparatively small areas of low pressure towards which winds blow. These winds blow obliquely owing to the rotation of the earth. The inswirl of air is counter-clockwise in the northern and clockwise in the southern hemisphere. There is a region of low-pressure calms in the centre of the system, because the air there is forced to rise upwards. Round this, perhaps extending for hundreds of miles, the outer air circles and forms winds. Such a system of winds and calm is called a cyclonic **depression**, and its centre is marked **low** on the chart.

Anticyclones are the opposite of cyclones. The centre is a region of high pressure from which winds blow. They move more slowly, as a rule, than cyclones, and often linger over a district for days or weeks at a time. The descending air causes a region of calms and settled weather. The centre of such a system is marked **high** on the chart.

These inswirls and outswirls of air move as a whole, and pass over the surface of the earth. They are more or less connected, and have what are called **hollows** and **ridges** between them. Depressions are separated by ridges, in which there are portions of high pressure. Hollows connect regions of atmo-

sphere where the pressure is low, and they separate regions of high pressure.

Weather Charts.

Cyclones and anticyclones are represented by lines called **isobars.** Isobars are lines on charts connecting places which have equal barometric pressure at a given time. They are drawn according to the information sent to the Meteorological Office by wireless and telegraph. Besides barometric pressure the observers send the temperature, winds, rainfall, kind of weather, state of the sea, etc., and this information is marked on a map. Such a map, when the isobars and other meteorological information is marked on it, is called a **weather chart.**

b	*bc*	*c*	*m*	*f*	*o*
Blue sky	Bright patches	Cloudy	Misty	Foggy	Overcast
d	*p*	*r*	*q*	*l*	*t*
Drizzle	Passing showers	Rainy	Squally	Lightning	Thunder
s	*h*	*rs*	*w*	*y*	*z*
Snow	Hail	Sleet	Dew	Hoar frost	Heat or dust haze

The chart has letters, figures, and arrows marked on it as well as the isobars, and very often a table

of references is given. Admiral Beaufort drew up a **notation** for general use, in which letters signify certain atmospheric conditions. A modified form, similar to the one given on the previous page, is often printed with charts.

Wind is shown by arrows, and very often a circle at the point of the arrow indicates the speed in miles per hour. Some arrows are feathered, and the number of feathers corresponds to the "Beaufort numbers" in the wind scale drawn up by Admiral Beaufort, or to a reference given with the map.

NUMBER OF FEATHERS	0	2	4	6	7	9	11	12
KIND OF WIND	Calm	Slight breeze	Moderate breeze	Strong breeze	High wind	Strong gale	Storm	Hurricane
AVERAGE SPEED IN M.P.H.	0	5½	15½	28	35	50½	69½	75

The amount of rain is often indicated by a circle containing a number, very often a fraction. Temperature and barometric pressure are shown by figures. In the case of pressure the figures at the ends of the isobars are often given in millibars as well as inches of mercury; 1,000 millibars correspond to 29·53 inches of mercury.

Weather Forecasts.

In Britain wind systems of a cyclonic nature generally come from the south-west. Their approach is usually foretold by the barometric **tendency** to

sphere where the pressure is low, and they separate regions of high pressure.

Weather Charts.

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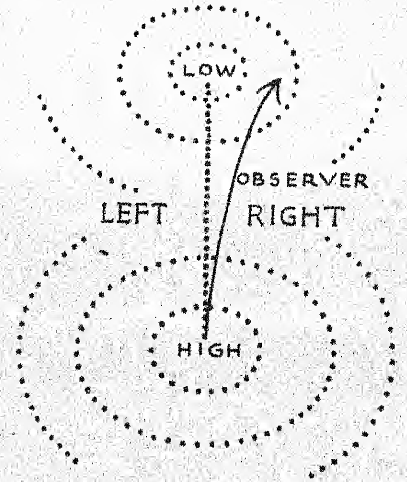
NUMBER OF FEATHERS	0	2	4	6	7	9	11	12
KIND OF WIND	Calm	Slight breeze	Moderate breeze	Strong breeze	High wind	Strong gale	Storm	Hurricane
AVERAGE SPEED IN M.P.H.	0	$5\frac{1}{2}$	$15\frac{1}{2}$	28	35	$50\frac{1}{2}$	$69\frac{1}{2}$	75

The amount of rain is often indicated by a circle containing a number, very often a fraction. Temperature and barometric pressure are shown by figures. In the case of pressure the figures at the ends of the isobars are often given in millibars as well as inches of mercury; 1,000 millibars correspond to 29·53 inches of mercury.

Weather Forecasts.

In Britain wind systems of a cyclonic nature generally come from the south-west. Their approach is usually foretold by the barometric **tendency** to

fall—that is, a steady decrease in the height of the mercury column is noticeable. The winds are noted, and by their direction the location of the region of low pressure is indicated. Buys Ballot's Law, discovered by a Dutch scientist and named after him, states that in the northern hemisphere, if we stand with our back to the wind, the *low* pres-



ILLUSTRATING BUYS BALLOT'S LAW.

sure area is on our left. The wind does not blow directly from high to low pressure, but, owing to the earth's rotation, is deflected to the right. Hence the region of low pressure lies ahead and towards the left of the observer. Thus an observer knows in which direction the centre of the cyclone lies, and he can tell it is approaching by the steady fall of the barometer. He can also tell when the centre has

passed, because his barometer begins to rise, and continues steadily rising. It is obvious that the **barometric tendency** is very important, and this, combined with a knowledge of Buys Ballot's law, is a great help in **forecasting**, or telling beforehand, what the weather is likely to be. From the information regarding winds, rainfall, kind of weather, etc., in certain regions, the passage of the disturbance can be described with fair accuracy. Its position at a known time can be given, and also its direction. Thus a forecast can be drawn up, and from the nature of the disturbance the weather that may be expected during, say, the next twenty-four hours can be communicated to all concerned.

Cyclones usually bring unsettled weather, gusty winds, sudden rain, often followed by calms. Anticyclones usually mean calm, settled weather, sunny and warm in summer, with fogs or mists in winter. The weather is usually dry, owing to the air settling downwards.

CHAPTER XXII

A TYPICAL BRITISH WEATHER CHART AND FORECAST

The Times publishes each day a weather chart, forecast, "flying prospects," and "sea passages" based on the Meteorological Office 6 p.m. reports of the previous day. The map reproduced opposite shows typical conditions of weather for December, and the symbols used are typical of those used on all weather maps.

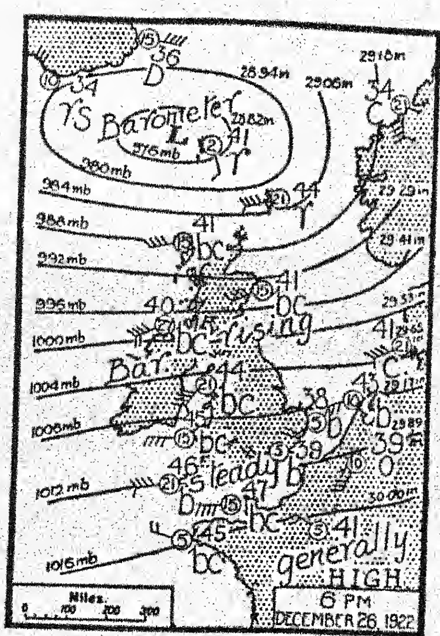
The *thick curved lines* are isobars marking the barometric pressure, which in this case is low to the north and high to the south of the British Isles. The lines are marked in millibars and inches of mercury, the lowest reading being 28·82 inches and the highest being 30·00 inches.

The direction and speed of the wind are marked by *arrows* having feathers and a circle. In the circle is a number indicating the speed in miles per hour, and the feathering refers to "Beaufort's Wind Scale." From the map it is seen that the wind is westerly over Britain, southerly in Norway, and then easterly, following a counter-clockwise direction generally. This is characteristic of a cyclonic "depression."

The *numbers* (34, 39, 41, etc.) are the temperatures in F.° at the places indicated.

The letters (*rs*, *bc*, *o*, etc.) indicate the kind of

weather according to the "Beaufort Notation," which has been previously given in this chapter. From the map it is seen that in the region where the pressure is lowest (L) and the air ascending in consequence, there is rain (*r*), drizzle (*d*), and sleet (*rs*).



A BRITISH WEATHER CHART AND FORECAST.

(Reproduced by permission of "The Times," London.)

The barometric "tendency" is shown as *rising* along the isobar marked 29·53 inches, and as *steady* along the isobar marked 29·89 inches.

The map represents an unstable type of weather, as shown by the forecasts which were made from it.

Forecasts for Wednesday, December 27.

(Twenty-four Hours from Midnight, Tuesday.)

1. General Inference from Observations at 6 p.m.—The depression to the northward of Scotland will maintain westerly winds generally over the British Isles. In the North showers of rain, hail, or snow will occur, with brighter intervals. In the South mainly fair weather may be expected, with local showers of rain or hail. Temperature will, as a rule, be moderate to rather low, and frost is likely in many places inland at night.

2. Special Forecasts.—England, S.E., E., S.W., Midlands, E., W., Wales, S., Ireland, S.E., S.W.: Wind westerly, moderate or fresh; mainly fair; local showers of rain or hail; visibility good; moderate day temperature; frost in places inland at night.

England, N.W., N.E., Midlands, N., Wales, N., Scotland, Isle of Man, Hebrides, Orkneys, Shetlands, Ireland, N.W., N.E.: Wind westerly, strong at times; bright periods; some showers of rain or hail, and, in places, of snow; visibility good; moderate to rather low temperature; frost in places inland at night.

3. Further Outlook.—Unsettled generally; considerable fair periods in the South.

4. Flying Prospects.—England, S.E., and Eastern Channel: Winds will be from between S.W. and W., averaging 20 to 30 m.p.h. in velocity at 2,000 feet, 15 to 25 m.p.h. near the surface at sea and on the coast, and 10 to 20 m.p.h. inland. Fine to fair weather is probable generally at first, but in the

course of the day conditions seem likely to revert to an unsettled type, with much cloud below 3,000 feet, and showers or rain at times in some parts of the area. Except for morning mists, visibility should exceed five miles, and no impediment to cross-country or trans-Channel flights need be anticipated.

5. Sea Passages.—English Channel: Wind between S.W. and W., averaging 15 to 25 m.p.h.; mainly fine to fair, then probably becoming unsettled, with much cloud and some showers or rain in places; visibility above five miles generally; sea moderate.

Irish Sea: Wind between W. and S., averaging 15 to 25 m.p.h.; weather varying from fair to dull, with showers or rain at times in many parts—perhaps hail locally; visibility mostly above five miles; sea moderate.

Information like the foregoing is published every day, and it is interesting to note the weather as forecasted and compare it with the actual weather which occurs. Forecasts are now recognized as of great practical use in everyday life and work, and if we are to be up-to-date we must have a knowledge of weather charts and their symbols. We also need to understand intelligently some of the natural phenomena we see each day and some of the causes of our daily weather. It will be found most helpful to watch the weather maps as they are published and notice the movements of the wind-systems as indicated by the isobars.

CHAPTER XXIII

THE TRUE PURPOSE OF KNOWLEDGE

Success.

ARE you still on friendly terms with the weather? Do the changing seasons still interest you? Is your record of the weather a living thing? Your record should grow, day by day, as the months pass. Let me remind you that the easiest and quickest road by which to learn is to do. That is why a *record* is so important.

You will find that practice makes perfect, and that what you do becomes part of yourself. Use your hands as well as your eyes, ears and mind, and become so interested in what you are doing that you want to **think things out for yourself.** Once you learn to do this you are on the way to success.

Clearer Vision.

The beautiful earth on which we live is just like a book full of most interesting pictures. We must learn to read this book as accurately as we can, and look at the pictures so that we can understand them.

But we may understand a picture without really seeing the beauty of it. We may see the details without catching the full view of the glorious masterpiece, and the inner meaning of it all. We

may be accurate in our methods of seeing details, and yet be in danger of losing sight of the great and noble whole.

We have intelligences which can be trained to be wonderfully accurate. But we were never meant to become merely accurate machines.

Is it too much to expect you to see the beauty of the clouds as well as give them their correct names? To wonder at the glory of the rainbow is the true complement to knowing how it is formed.

And surely we shall not stop at a sense of the beautiful, and those beginnings of adoration which have their sources in wonder. Is there not something else? What more can we see in it all?

The Purpose of Knowledge.

John Ruskin, who saw so much of the truly beautiful, wrote the following words, which should be remembered by all who have learned something of the natural phenomena in the world in which we live. He said: "All knowledge is lost which ends in the knowing, for every truth we know is a candle given us to work by. Gain all the knowledge you can, and then use it for the highest purpose."

And what purpose is highest in life? Is it not to serve God and our fellow-men by making the conditions under which men live as beautiful as possible, and by teaching men to see beauty in life, in nature, and in nature's God?

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PREFACE.

DURING many years' experience in teaching practical chemistry to students who have completed a course of elementary work, the authors have felt the need of a laboratory manual more general in character than those commonly used. The preparation of inorganic compounds is a very important branch of experimental work which is too often neglected, but which forms a most valuable preliminary to the study of the analytical methods adopted for the detection and separation of the elements.

In this volume a selection has been made of typical preparations which can easily be carried out by a careful student. The methods described have all been repeatedly practised in the authors' laboratories, and found to yield satisfactory results. A number of simple organic preparations has also been added. While full instructions are given, so as to render it possible for a student of little experience to work by himself, it has been assumed that the work will be supervised by a teacher.

The arrangement of the inorganic preparations is not necessarily that in which they should be taken; this must be left to the discretion of the teacher. But it would be well for a student beginning the study of organic chemistry to work through the organic part in the order given.

Some knowledge of elementary chemistry is expected to be possessed by students using this book. In order, however, to facilitate the work of those who have not much laboratory experience, an introductory section has been included, containing a short account of the apparatus and appliances required for the work which follows, and commonly found in laboratories.

The section on Qualitative Analysis has been made sufficiently complete for most practical purposes, and should be undertaken after the preparation of inorganic compounds. Some knowledge of organic chemistry, however, will be required for a proper understanding of the reactions and detection of the organic acids.

Quantitative work is dealt with in a simple manner in Part II. of the book, and here also a short account of the principles underlying quantitative analysis, and of the apparatus employed in carrying out the work, has been included in the introduction. The sections on Volumetric and Gravimetric Analysis are intended to serve only as a short introduction to these branches of Quantitative work.

It is hoped that the book will be found useful by teachers, and by students preparing for the various University examinations in Practical Chemistry, the examinations of the Board of Education, the Pharmaceutical Society, and other bodies.

J. B.
H. H.

CONTENTS.

PART I.

PART II.

PART I.

INTRODUCTION.

1. Glass tube. It is necessary frequently to cut and bend glass tube in the fitting up of apparatus. For connections, soft glass, that is, readily fusible glass, of small diameter, is generally employed. To break this, make a cut with a sharp file at the required position; hold the tube firmly in both hands, pressing the thumbs together on the glass opposite to the cut, and pull the hands apart. The tube will break evenly at the cut. For wider tube this will be found difficult; it is better to make a deep cut on one side of the tube, and apply to it a red-hot point of glass. The tube will crack all round, or partly so. In the latter case, apply the hot point to the end of the crack and so lead it all round the tube. The glass-cutter (Fig. 1) is very effective for glass tube of all kinds. By rotating the tube in the cutter, the edge of the steel wheel makes a circular cut, and with this even hard combustion tube can easily be broken.

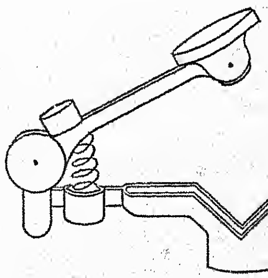

Fig. 1.

2. To bend glass tube. Hold the tube in the upper part of the flame of a fish-tail burner, and in the same plane with it, and rotate the tube slowly and continuously on its axis, so that it is uniformly heated (Fig. 2, *a*). When it becomes soft, remove it from the flame and bend it to the required angle.

The bend should then appear as Fig. 2, *b*. If the tube is heated in a Bunsen burner, only a short length becomes softened, and it then bends like Fig. 2, *c*. This is much weaker than the proper bend, and is liable to break under a slight stress.

To draw out glass tube to a capillary, the tube is first softened in the Bunsen burner, with continued rotation, then removed from the flame and the two portions drawn apart until the capillary is of the required diameter. If the capillary is to have a thick wall, the tube must be kept soft in the flame, before drawing, until the wall has thickened sufficiently.

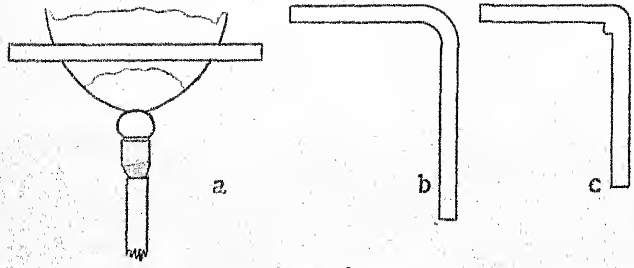

Fig. 2, *a. b. c.*

To seal the end of a tube, it is best to draw off a portion as just described, and then, in a small flame, draw off the narrow portion where the narrowing just begins. In this way the inside of the tube is kept free from moisture.

For hard Jena glass or combustion tube, the blow-pipe flame will be required, and for the hardest combustion tube, the oxy-coal gas flame. The blow-pipe flame may be made much more effective by allowing it to impinge on a vertical firebrick slab, placed just behind the article to be heated. The heat is thus to some extent conserved.

3. Corks and cork-borers. Corks should be made of sound bark only. Before use they should be well softened in the cork-press, or by rolling under a flat weight. To bore the cork, a borer should be selected slightly less in diameter than the tube to be inserted. Begin at each end of the cork and bore half-way through, rotating the borer on its axis and

applying only a slight pressure. With a little care the holes will meet midway. Subsequent filing of the hole is not to be recommended, as this seldom gives a gas-tight joint.

Rubber stoppers may be bored similarly, but the hole should be made from one end only. The borer should be a little larger than the hole required, and should be lubricated with caustic soda solution or glycerine. The borer must also be sharp. It may be sharpened by rubbing the outside of the edge with a file, but better results are obtained by using the special sharpener.

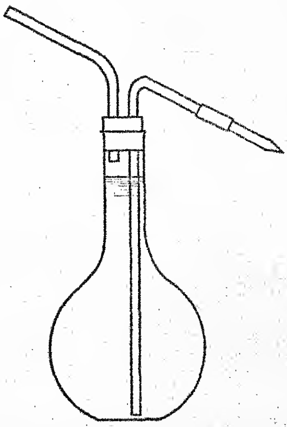

Fig. 3.

4. To fit a wash-bottle. The construction is shown in the diagram (Fig. 3). A rubber cork gives a more gas-tight apparatus, but should not be used with organic liquids, as alcohol, ether, etc. When using unpleasant-smelling liquids like sulphuretted hydrogen water, a rubber tube may be placed on the end of the glass tube, air blown in and the rubber then closed by the finger and thumb. The stream of water will continue for a short time. The pressure on the tube should be released before again applying the mouth.

SOLUTIONS.

5. Preparing a substance for solution. Materials that occur in large crystals should be ground to a more or less fine state of division in a Wedgwood or porcelain mortar (Fig. 4). The process of solution will then be much more rapid, whatever the solvent may be. For hard materials an iron mortar may be used, but there is some risk of contamination

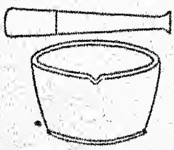

Fig. 4.

with iron, and in quantitative analysis this is to be avoided. Minerals, which must be reduced to an impalpable powder before the treatment with the acid to obtain a solution for analysis, may be crushed to small pieces in the steel crusher (Fig. 5). This consists of three parts. The hollow cylinder fits into the cavity in the base, and the ram fits into the cylinder. The mineral is placed in the latter, and the ram hammered in. The coarse powder so obtained is then very finely ground in the agate mortar (Fig. 6). To obtain the finest powder, a very small quantity is ground at one time, until the gritty sensation can no longer be detected.

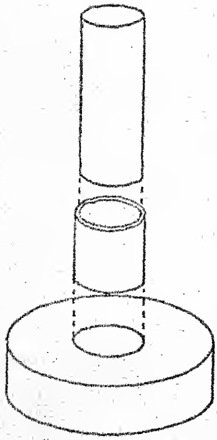

Fig. 5.

6. Making a solution. In general it is sufficient to bring the substance, in a sufficiently fine state of division, and the solvent together in a beaker or flask, stirring or shaking frequently, and heating if necessary on the water-bath. The stirring, if it has to be long-continued, may be effected by means of a water-turbine (Fig. 11).

When a volatile solvent like alcohol or chloroform is being used, the solution should be made in a flask fitted with a reflux condenser, and heated on the water-bath (Fig. 18).

To ensure that a solution is saturated, there must be some of the substance (the solute) remaining undissolved when the operation is over.

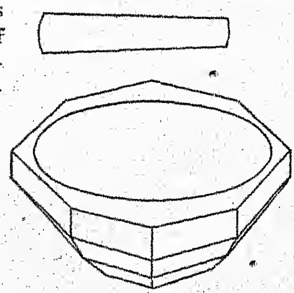

Fig. 6.

SOLUBILITY.

7. The solubility of a substance varies with the temperature, increasing in the majority of cases with increase of temperature. All

determinations must, therefore, be made at a definite temperature, which must be kept constant while the solution is being prepared.

The **thermostat** is an apparatus for this purpose. It consists of a water-bath of sufficient magnitude, the water being kept gently moving by means of a current of air from a tube let down to the bottom, or by some form of mechanical stirrer. The temperature is kept constant by interposing a **gas-regulator** between the gas-tap and the burner. There are many forms of regulator. A simple one, Reichardt's, is shown in Fig. 7. The bulb of mercury is clamped in the bath. The gas passes in at *a*, enters the opening at the bottom of the hollow ground-in stopper, and passes from the latter at *b* to the burner under the bath. Should the temperature rise, the mercury expands and partially closes the sloping opening at the bottom of the stopper, thereby diminishing the gas-supply and lowering the flame. A fall of temperature results, with opposite effects. In this way the temperature of the thermostat can be kept within very narrow limits, say half a degree, this depending on the construction and sensitiveness of the regulator, size of bath, etc. For different temperatures the amount of mercury is varied by means of the brass screw at *c*. A small by-pass prevents extinction of the flame.

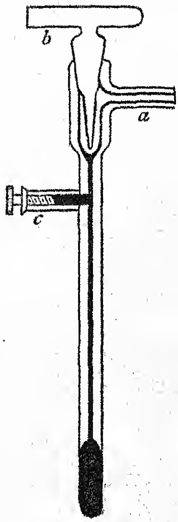

Fig. 7.

8. To determine solubility. The material to be examined is placed, together with the solvent, in a flask or bottle, which is then closed, immersed in the thermostat, and frequently shaken or kept in motion mechanically. After an hour or more a portion of the clear liquid is poured into a weighed, stoppered bottle, allowed to cool and weighed. The amount of dissolved substance is then determined by a chemical analysis, or by evaporating and weighing the dry residue.

The relation of solubility to temperature may be shown

graphically by means of curves like those in the diagram[1] (Fig. 8). Nearly all exhibit a regular increase, the curves for sodium chloride and potassium iodide being almost straight lines. In the case of anhydrous sodium sulphate the solubility attains a maximum at 33°, and then diminishes.

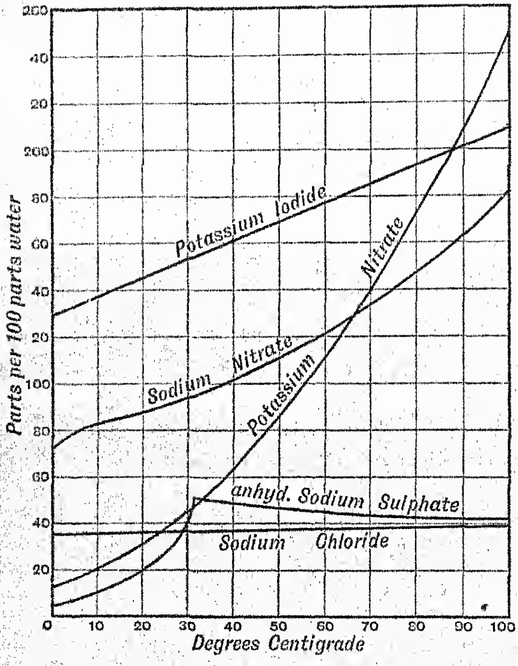

Fig. 8.

As an example, determine the solubility of potassium dichromate at various temperatures, and draw the solubility curve. Begin with a solution saturated at 80°—90°, by immersing in a large beaker of water. The gas-regulator may be dispensed

[1] The data for these curves are taken from Comey's *Dictionary of Chemical Solubilities.*

with. Decant a portion into the weighing-bottle, allow to cool, weigh, then wash out into a weighed porcelain dish, evaporate to dryness on the water-bath, and heat gently with the naked flame until the weight is constant. Allow the remainder of the liquid to cool, take off portions at 60°, 40°, etc., and proceed as before. From these weights the solubility may be calculated at once, in grams of dry solid per hundred grams of water.

CRYSTALLISATION.

9. From the above solubility curves it is obvious that if a solution, say of potassium nitrate, saturated at 80°, and containing therefore 172 grams of solid per 100 grams of water, be cooled to 20°, the liquid then retains only 31.2 grams per 100 grams of water. A quantity of nitrate therefore, 140.8 grams, must separate from the liquid. This separation of a dissolved substance on cooling a solution saturated at a higher temperature generally takes place in forms of definite shape, called crystals, and the process is called crystallisation.

10. Purification by crystallisation. If the original substance contains a soluble impurity, this may be wholly or partly removed by crystallisation. If the impurity does not saturate the liquid at the lower temperature, it will all remain in the mother liquor, and the crystallised substance will therefore be free from it. The degree of purification thus depends on the amount and solubility of the impurities, and repeated recrystallisation is sometimes necessary to obtain a pure product.

In cases where a substance is much less soluble in the cold than in the hot solvent it may be obtained in the form of very small crystals ("meal") by rapidly cooling a hot saturated solution, stirring or shaking meanwhile.

11. Fractional crystallisation. In the case of two substances of different solubilities, the less soluble will crystallise first, with only a small amount of the more soluble. A solution, made from the product thus obtained, will by a second crystallisation yield a less impure substance. The product should always be tested for the more soluble substance, and if this is found, the process should be repeated.

By fractional crystallisation, substances having similar solubilities may be separated if one is present in much larger quantity than the other.

A separation may often be effected by pouring off the liquor from the first crop of crystals, before it has cooled to the temperature at which it is saturated with the second substance. The latter will then crystallise on further cooling, together with some of the first substance.

The table of solubilities given in the appendix will be found useful in the above operations.

Certain substances crystallise together in the form of double salts, *e.g.* ferrous sulphate with ammonium sulphate to form ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4+6H_2O$. Such compounds cannot be separated by this method.

12. Isomorphism. Substances of similar chemical constitution, having an equal number of atoms in their molecules, and crystallising in the same form, are termed **isomorphous.** They often have certain elements in common, and show analogous properties. Such substances have also the property of mixed crystallisation, that is, the crystals separated from a solution of two such bodies contain a mixture of the isomorphous compounds, even when the concentrations of the two bodies in the solution differ considerably. Such compounds, therefore, cannot be separated by crystallisation.

The law of isomorphism was discovered by Mitscherlich in 1820, by an examination of the corresponding salts of phosphoric acid, H_3PO_4, and arsenic acid, H_3AsO_4. Examples will be given later, in the alums, etc.

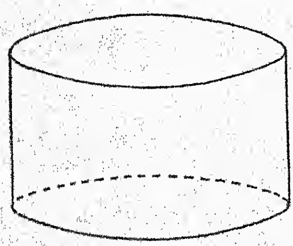

Fig. 9.

13. Growth of crystals. By slow evaporation of the solvent larger and purer crystals are obtained. This may be effected in a shallow flat-bottomed crystallising dish (Fig. 9). The small crystals which separate first from a solution are usually perfect. If such crystals are suspended in the saturated solution by a hair or silk fibre, or if they are turned every day

on different faces, so that all are equally exposed to the action of the solution, large and perfect crystals can readily be obtained. In a crystalline mass, however, the individual crystals are usually incomplete or distorted.

PRECIPITATION.

14. When solutions are mixed containing two bodies which can, by interaction, produce another substance insoluble or sparingly soluble in the solvent, then, in general, this other substance is produced, and separates from the liquid in the form of a **precipitate**. Thus when barium chloride and sodium sulphate are dissolved separately in water, and the solutions mixed, barium sulphate is at once separated as a white precipitate, this being practically insoluble in water.

Precipitation may take place slowly or rapidly, and is less or more complete, according as the precipitated substance is more or less soluble in the solvent. A change in the composition of the solvent often brings about precipitation or rapid crystallisation, as, for example, in the purification of common salt (par. **28**) by dissolving hydrochloric acid in its saturated aqueous solution, the addition of water to the alcohol in the preparation of iodoform (**117**, 5; **129**), or the addition of alcohol in the precipitation of lead sulphate (**303**). The rate of precipitation is often increased by vigorous stirring or shaking in a tightly stoppered precipitation jar (Fig. 10). In all cases the solution should be constantly stirred while the precipitant is added, to ensure thorough mixing. A large excess of the precipitant should be avoided, when possible, in order to facilitate the subsequent washing.

Fig. 10.

When the solubility of the precipitate is not appreciably increased by heating the liquids, it is often advisable to do this; the result is to render the precipitate more granular. Many precipitates also which are produced at first in a gelatinous form, as magnesium ammonium phosphate from strong solutions, become crystalline on standing for some hours. This is very

important with regard to the subsequent filtration, as a crystalline or granular precipitate is always more easily and rapidly filtered and washed than one of a gelatinous or coherent nature.

When a large quantity of material has to be dealt with, or when the precipitation occupies some time, the stirring or shaking may be done by means of a water-turbine (Fig. 11), electric motor or hot-air engine. The first of these is generally avail-

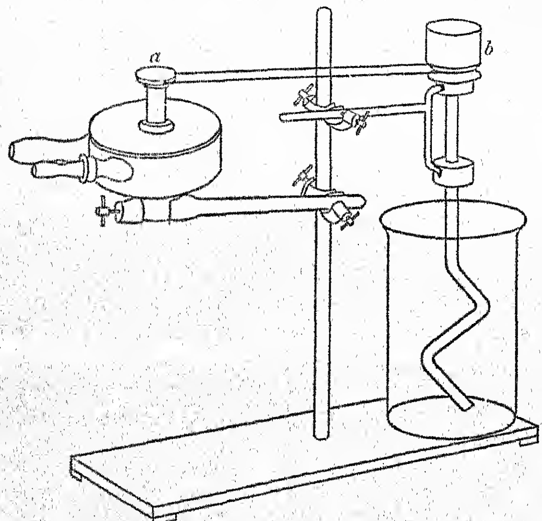

Fig. 11. (Turbine, etc.)

able. The small wheel *a* of the turbine is coupled by means of a thin cord or rubber band to the wooden pulley *b*, in which the bent glass rod stirrer is firmly fixed.

FILTRATION.

15. Before filtering off a precipitate it is in general advisable to allow it to settle, and to filter the clear liquid first. The precipitate may then be washed by **decantation**, that is by

mixing it with fresh solvent and again allowing to settle, after boiling if necessary to facilitate the removal of the impurities.

For the large quantities of liquid employed in preparations, a cloth bag filter may be used, made of stout calico and supported on a wood frame. It is also useful to employ a **fluted** filter of paper. This is made by folding the paper into 8, 16, or 32 folds according to the size of paper, instead of 4, and then arranging the folds alternately inwards and outwards. The filter is then arranged in a series of ridges meeting at the apex. This ensures more rapid filtration.

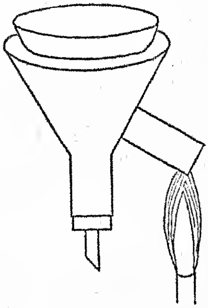
Fig. 12.

When it is desirable to filter a hot, nearly saturated solution, the filter funnel must be kept hot to avoid crystallisation of the substance. This may be done by placing the funnel in the hot water jacket (Fig. 12), passing the stem through a good cork in the bottom of the jacket.

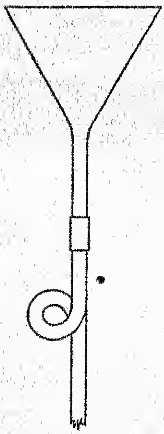
Fig. 13.

Filtration may be hastened in several ways. In analysis it often saves time to place a small fall-tube (Fig. 13) on the end of the funnel. This can easily be made by softening a glass tube in a large flame and then bending it into a complete circle. The lower straight piece should be six or seven inches long, the upper one short.

16. **Filter pumps** are commonly used to accelerate filtration. The upper end of the pump (Fig. 14), which may be of glass or metal, is firmly connected to the water-tap by means of strong pressure tube, secured by copper wire. The water issues through the narrow jet *a*, and at a high speed enters the slightly wider upper end of the lower tube, forcing the air down this tube in its flow. The bendings in this tube are intended to obstruct the backward passage of air. A diminished pressure is thus created

in the bulb of the pump, and in any vessel connected with it by means of the side tube. These pumps are very useful for vacuum distillation, and the pressure can readily be reduced to 10-12 mm.

The pump flask *b* shown in the diagram is of strong glass, and the Buchner funnel *c* is made of porcelain, with a flat per-

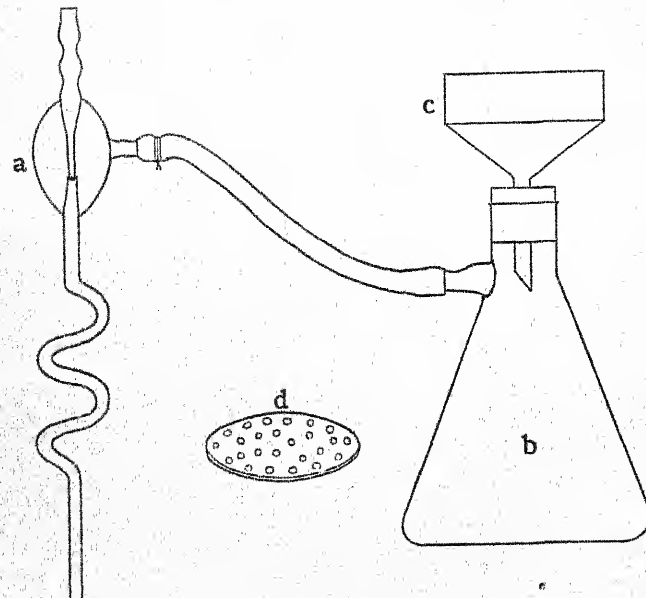

Fig. 14.

forated bottom which is either of one piece with the funnel or detachable. An ordinary glass funnel may be used, and the perforated porcelain plate *d* inserted.

The perforated bottom or plate is covered with filter paper or linen, cut to the required shape. This is then moistened with water, and pressed down so that the edge is completely closed. The pump should be working slowly while this is done. To

stop the pump when filtration is over, *first detach the tube* from the pump flask, and then turn off the water. If the water is first turned off, some may run into the pump flask on account of the low pressure therein.

17. Washing precipitates. As already explained, this may be done partially in the precipitation vessel by decantation. The liquid in each washing should be run off as completely as possible before adding the next. This applies also to the final washing on the filter. Suppose that in good and defective working respectively one-tenth and one-half of the liquid is left each time when the next washing is added. Then after three washings the concentration of the impurity is reduced in the first case to one-thousandth, in the second case to one-eighth only of its original value.

When the material to be filtered is soluble, as in the preparation of crystallised salts, the quantity of solvent used for washing must of course be as small as possible.

When the pump is being used for filtration, it must not be at work when the washing is done. Detach the tube from the pump flask, add the washing liquid to the funnel, and gently mix it with the upper portion of the substance, taking care not to disturb the filter cloth. Then allow the liquid to percolate through the mass by gravitation, and use the pump only to complete the draining. In this way the whole mass of the material is washed by the liquid. If the pump is constantly at work, the washing liquid is simply drawn through the mass by the easiest route, and the washing is consequently incomplete.

To make the draining off of the liquor as complete as possible, the substance in the funnel may be pressed down by aid of a flattened glass rod, or the top of a flat glass stopper.

ASPIRATORS.

18. These are employed for various purposes in which a slightly reduced pressure is required, as *e.g.* for drawing a current of air through an apparatus or a liquid, to assist filtration, etc. They are of various forms, some of which are shown in the diagrams. An ordinary glass bottle may be employed (Fig. 15, *a*), fitted with stopper and two tubes. Water is run

from the bottle by the longer tube, which acts as a syphon, and air is drawn in by the shorter tube. The second form, *b*, acts

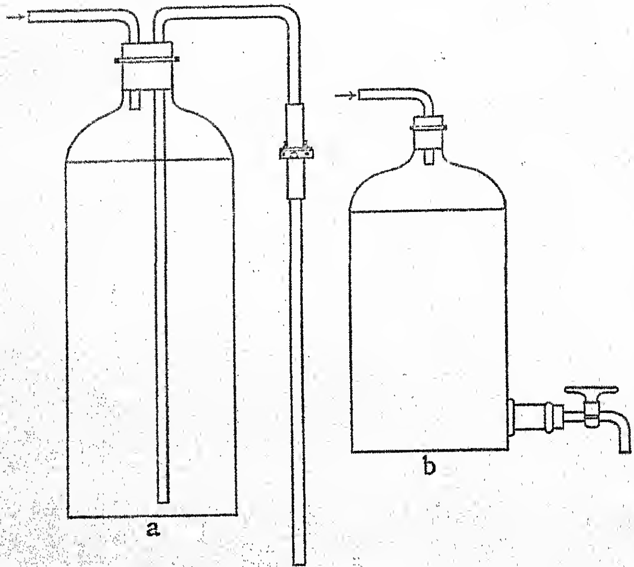

Fig. 15.

similarly, the water being drawn off by the glass tap at the bottom. A small aspirator may be made at once by simply inverting the wash-bottle (Fig. 16), and allowing the water to run off by the short tube. A screw clip on the rubber tube regulates the flow of the water.

These aspirators are, however, intermittent in action, and not of great power. The most generally useful, and at the same time the most powerful and continuous for ordinary laboratory use, is the water pump already described (Fig. 14).

By means of the water pump also, a current of air under increased pressure may be obtained. The arrangement is shown in Fig. 17. Water and air together are forced into the bottle by

the pump. The water is run off at the bottom, and the compressed air escapes by the side tube at the top of the bottle. This

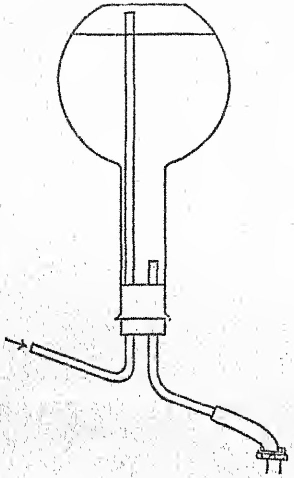

Fig. 16.

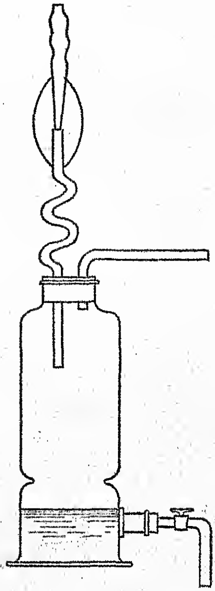

Fig. 17.

current of air can be made powerful enough to work an ordinary gas blow-pipe.

EVAPORATION.

19. In many cases a liquid may be evaporated by boiling it in an open vessel, preferably one which gives the liquid a large surface, without detriment to, or loss of, the dissolved substance. Porcelain dishes are usually employed for this purpose.

Evaporation may also be carried on more slowly, by heating on a steam-bath. A simple steam-bath may be made by boiling water in a beaker, and placing the dish containing the liquid on the mouth of the beaker.

A water-bath, strictly regarded, is one in which the vessel to be heated is immersed in the water. Such baths are often employed, as *e.g.* in determining solubilities as described earlier. But the term is also applied to all kinds of steam-baths in which the steam is generated from water in the same bath.

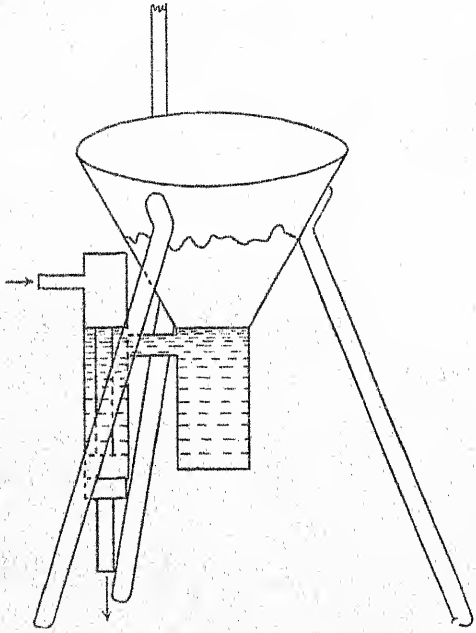

Fig. 18.

One of the most convenient forms of such water-baths for the working bench is shown in Fig. 18. As indicated in the diagram, the amount of water required is small, and this admits of rapid heating. The constant-level arrangement at the side obviates the risk of boiling to dryness. A series of concentric rings of copper or porcelain on the mouth of the bath makes possible the accommodation of vessels of different sizes. Lastly,

one of the legs is continued in the upright iron rod, on which a clamp may be held for the support of a reflux condenser.

Evaporation may also be carried on by distillation, with condensation of the solvent if this is of value.

When it is desirable to evaporate a liquid rapidly without much increase of temperature, this may be done by distillation under diminished pressure, at the ordinary temperature or a little over it. In this case the liquid is contained in a strong, round-bottomed flask, and a tube drawn to a fine capillary passes into the liquid. For receiver a distilling flask or pump flask is taken, and this is exhausted by the pump, with an interposed empty bottle in case of accident from a back-flow of water. The capillary above referred to admits a stream of minute air-bubbles through the liquid, which secures regular boiling.

The vacuum desiccator (Figs. 19, 20), may also be used for rapid evaporation at the ordinary temperature.

DRYING.

20. Desiccators. A desiccator is a vessel in which a dry atmosphere can be maintained, and which can be made gas-tight.

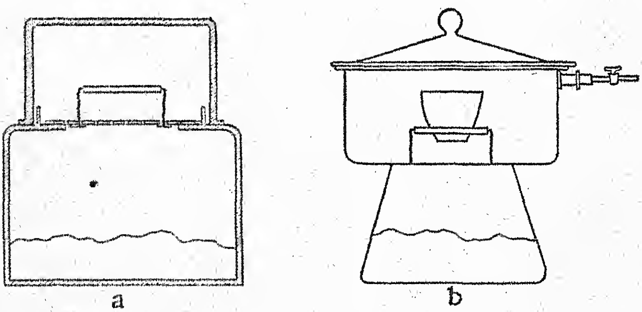

Fig. 19.

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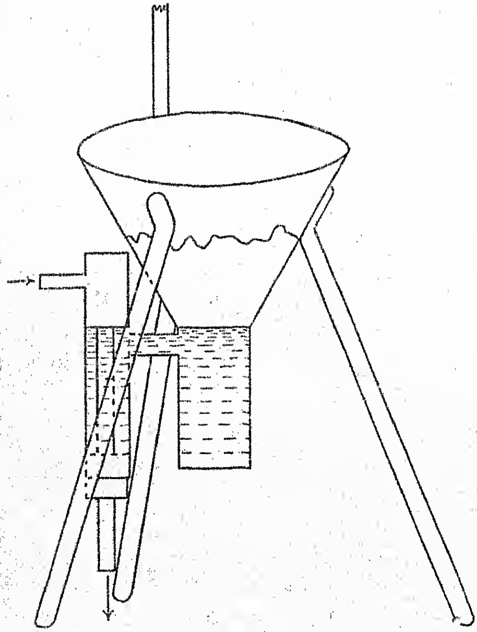

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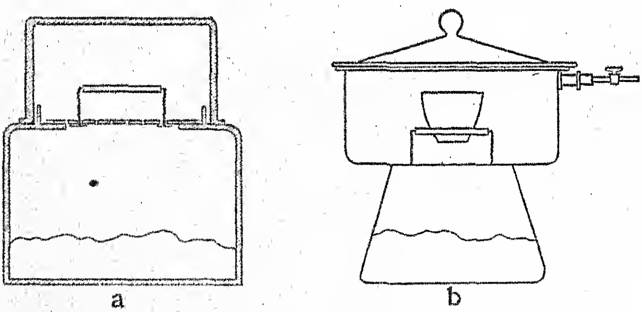


Fig. 19.

It is employed for a variety of purposes. Crucibles are allowed to cool, before weighing, in the desiccator; weighing bottles

containing substances for analysis may be kept therein; crystals may be dried, or liquids evaporated, especially in the vacuum form of apparatus. Two forms are shown in Fig. 19, and a third in Fig. 20. The drying agent, sulphuric acid, with or without pumice, or anhydrous calcium chloride, is placed in the lower part of the vessel. Calcium chloride is preferable to a liquid, in an apparatus which has to be carried to and fro, and for vacuum desiccators sulphuric acid should not be used. The

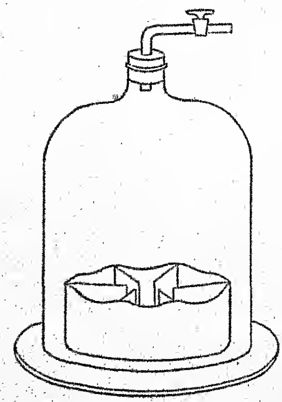


Fig. 20.

under edge of the cover is slightly greased. The bell-jar (Fig. 20) has the lower rim well ground, and stands on a thick ground glass plate. The drying agent is placed in the porcelain trough, on which a dish or crucible may be laid. The bell-jar is closed by a stopper and glass tap, so that, like Fig. 20, *b*, it may be exhausted, and the tap then closed. A good vacuum desiccator should preserve the vacuum for several days, but this should be tested, and the exhaustion repeated.

The drying of a solid substance may be assisted greatly by spreading it on a **porous clay plate**, especially if it be finely divided and retentive of moisture. The clay absorbs the

water slowly; the drying may be further accelerated by placing the plate in the vacuum desiccator.

21. Ovens. For drying at higher temperatures, water, steam or hot-air ovens are employed. The construction of a water-oven is shown, partly in section, in Fig. 21. It consists of a double-walled box, usually made of copper, the water being contained in the space between the walls. The glass gauge at

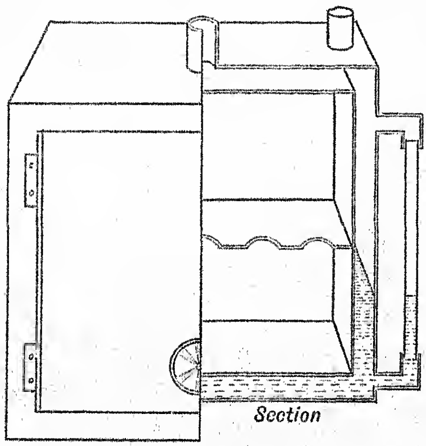


Fig. 21.

the side shows the level of water. A constant-level device may also be fitted.

The steam oven is of similar construction, the steam circulating through the space between the inner and outer walls. A number of these ovens are generally built together, the steam-space surrounding each compartment.

For temperatures below or above 100°, similar ovens may be used, with other liquids, or hot air may be circulated through the walls.

The air-oven (Fig. 22) need be only a simple box, and is made of sheet copper or iron. The outside is sometimes covered

with asbestos board to diminish the loss of heat. A thermometer is inserted in the top, and the temperature may be kept constant if desired by using a thermo-regulator such as that already described (Fig. 7, par. 7).

Great care must be exercised in the drying of all substances which are affected by heat, as, *e.g.* salts containing water of

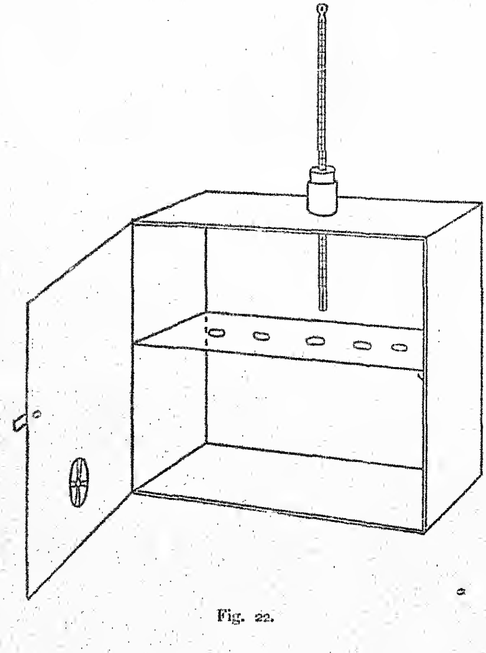


Fig. 22.

crystallisation. Such bodies must, in general, be dried at a low temperature.

22. The drying of gases. The operations of washing and drying gases are continually used in the laboratory, the general procedure being to bubble the gas through the liquids in wash-bottles. An ordinary bottle fitted as shown in Fig. 23, *a*, will serve for this purpose. A ground-in top carrying the two

tubes is often fitted. This has the advantage of being entirely made of glass, but the stopper is sometimes loosened by the pressure of gas. A better form is the Drechsel wash-bottle

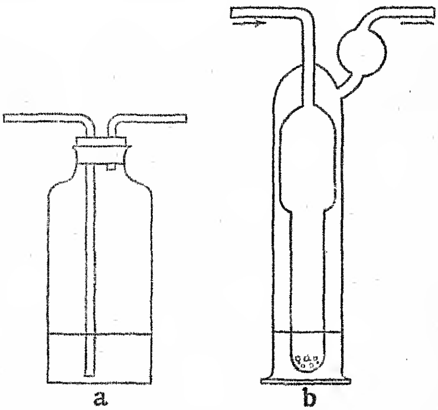


Fig. 23.

(Fig. 23, *b*), which is all of glass and in one piece. The entrance tube is widened inside, so that in the event of a back-pressure the liquid cannot reach the upper part of the tube.

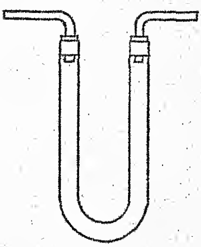


Fig. 24.

Water may be used for removing soluble impurities from gases which are themselves sparingly soluble in water. If the gas is soluble in water, its saturated solution may be employed to wash it. For drying, sulphuric acid is generally useful.

To ensure efficient washing or drying, however, it is not enough to use wash-bottles in this manner. The gas should be passed through large U-tubes (Fig. 24) which are filled with chips of pumice or glass beads, drenched with water for washing, or with sulphuric acid for drying. Calcium chloride may be used

for drying most gases. For ammonia, caustic potash or quick-lime in small pieces is used, and these may be placed in the eprouvette (Fig. 25), resting on the perforated lead

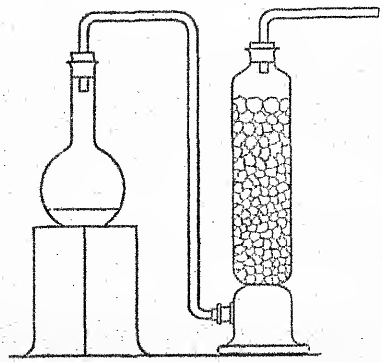


Fig. 25.

plate. For the most complete drying phosphorus pentoxide is used, and should be dusted over the glass beads in the U-tube, so that the passage does not become stopped by the pasty metaphosphoric acid.

SECTION I.

PREPARATIONS.

INSTRUCTIONS TO STUDENTS.

BEFORE commencing a preparation make certain that you understand the reactions involved. Read carefully through the whole of the instructions, and if anything is not clear, have it explained before proceeding. The quantities of materials to be used are in most cases given. Compare them with the formula weights, and if the proportions do not agree, that is, if an excess of one or other material is employed, find out why this is so.

In cases where an apparatus has to be devised, or put together from a description in the text, make a drawing of the apparatus you propose to use, and submit it for approval. When the apparatus has been fitted up, do not commence the experiment until it has been examined and approved by the teacher. In all cases follow carefully the instructions given.

Enter all work in the note-book at the time of observation, leaving nothing to be written up afterwards from memory. If your observations do not agree with the text, make a note of the fact. Weigh all finished products, and note the amount in your book. Calculate wherever possible the theoretical yield of product from the quantity of the original substance used, and deduce the percentage of the theoretical yield obtained in your experiment. Make a note, so far as you can, of reasons for the deficiency.

Before throwing away any liquors or residues, consider carefully whether you can make any further use of them.

A. INORGANIC COMPOUNDS.

THE ALUMS.

23. The alums have the general formula

$$R_2SO_4 . M_2(SO_4)_3 . 24H_2O,$$

where R is a monovalent element or group and M may be either aluminium, iron, chromium, manganese, etc. The alums are all isomorphous.

Crystallisation of Potash Alum.

$$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O.$$

Weigh out 200 grams of potash alum, dissolve in water, filter if necessary and allow to cool. If crystals separate on cooling, add water to dissolve them. Allow the solution to stand in a large crystallising dish (Fig. 9), covering the dish with a sheet of paper to protect the solution from dust. From the crystals first formed pick out those free from adhering crystals. Transfer the clear solution to a similar dish, place the selected crystals in it and allow them to grow. Each day if necessary remove the selected crystals and place in the clear solution as before, after redissolving any smaller crystals which may have separated. The crystals will be octahedral in shape, but unless turned (par. **13**) on different faces, to allow each face the same opportunity to grow, irregular octahedra will be obtained.

The 200 grams of alum may be replaced by molecular proportions of potassium sulphate, K_2SO_4, and aluminium sulphate, $Al_2(SO_4)_3 . 18H_2O$.

9·5 grams of potash alum dissolve in 100 grams of water at 10° C.

Alum is chiefly used as an aluminium mordant in dyeing.

Crystallisation of Chrome Alum.

$$K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O.$$

The solution obtained in the preparation of aldehyde may be used (par. **120**), or one prepared by passing sulphur dioxide into

a solution of 50 grams of potassium dichromate and 20 grams of sulphuric acid in one litre of water, until the reduction is complete. The temperature should not exceed 60-70° C. during the reduction and subsequent crystallisation. Otherwise the alum is obtained in the green modification, which is more soluble and more difficult to crystallise. The crystals are obtained as in the previous preparation. They are isomorphous with those of potash alum (compare them) and crystals of either substance, when placed in a solution of the other, will continue to grow (par. **12**).

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

The crystals of chrome alum are deep violet in colour, and are efflorescent. They melt in their water of crystallisation at 89° C.

Chrome alum is used as a chrome mordant, and in chrome tanning.

Ferrous Ammonium Sulphate.

$$FeSO_4 . (NH_4)_2SO_4 . 6H_2O.$$

24. Dilute 50 c.cs. of concentrated sulphuric acid to 200 c.cs., pouring the acid into the water in small quantities at a time. The mixture should be continually shaken. Divide the solution into two equal parts. Neutralise one part with ammonium hydrate, boiling to expel any excess of ammonia, and warm the other with iron filings (in the fume cupboard) till no more iron will dissolve. Filter the solutions into the same crystallising dish, add a few ccs. of dilute sulphuric acid to keep the solution clear and prevent the formation of basic sulphate of iron, and allow to crystallise.

$$H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + 2H_2O.$$
$$H_2SO_4 + Fe = FeSO_4 + H_2.$$

The substance may be purified by recrystallisation.

Molecular proportions of ferrous sulphate, $FeSO_4 . 7H_2O$, and ammonium sulphate, $(NH_4)_2SO_4$, may be used.

Ferrous ammonium sulphate crystallises in transparent bluish-green monoclinic crystals, and, being stable in the air, is used for the standardisation of solutions used in the volumetric estimation of iron. 17·5 grs. of the salt dissolve in 100 grs. of water at 12° C.

Iron Alum.

$K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$.

25. Weigh out one molecular proportion of potassium sulphate and two of ferrous sulphate, dissolve in water, filter into the same evaporating dish, add 6 c.cs. of strong sulphuric acid and 4 c.cs. of strong nitric acid. Boil until the solution which is at first brown (see explanation of brown ring test) becomes pale yellow. Evaporate to saturation point and crystallise at a low temperature.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

Iron alum crystals are isomorphous with those of the other alums. They are of a pale violet colour, and when exposed to dry air effloresce and form a basic salt of iron. The substance is chiefly used as an iron mordant.

Nickel Potassium Sulphate.

$NiSO_4 . K_2SO_4 . 6H_2O$;

and

Copper Ammonium Sulphate.

$CuSO_4 . (NH_4)_2SO_4 . 6H_2O$.

26. Prepare these salts from molecular proportions of the sulphates and compare the crystals with each other and with those of ferrous ammonium sulphate.

Potassium Nitrate.

KNO_3.

27. Weigh out molecular proportions of potassium chloride, KCl, and sodium nitrate, $NaNO_3$, dissolve the mixture in boiling water, evaporate till crystals of sodium chloride begin to settle out, filter hot and allow to cool. Crystals of potassium nitrate form and may be purified by recrystallisation. The mother liquor should be evaporated for a second crop of potassium nitrate crystals.

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

As Chili saltpetre contains chlorides, bromides, iodides and sulphates of sodium and magnesium with traces of iron salts, it should first be purified, or a pure sodium nitrate used.

The student should note the following solubilites :

	At 15° C.	At 100° C.
KNO_3	26·2	247
KCl	33·4	59
NaCl	35·9	39
$NaNO_3$	83·5	180

Potassium nitrate crystallises in long rhombic prisms. It is largely used in pyrotechnics, in making gunpowder and other explosives, and in the laboratory as an oxidising agent.

Purification of Common Salt.

28. Make 500 c.cs. of a saturated solution of common salt in water. Place the clear solution in a wide beaker and pass in hydrochloric acid gas. Owing to the great solubility of the gas in water, the liquid must be prevented from rushing back into the generator.

This may be effected by delivering the gas from the mouth of an inverted funnel dipping just below the surface of the liquid. Sodium chloride is precipitated owing to its slight solubility in a strong solution of hydrochloric acid, but magnesium chloride, the chief impurity, is much more soluble and is not precipitated.

Filter by suction, wash with pure concentrated hydrochloric acid, partially dry with filter paper, then in the air oven, and finally by heating in a porcelain dish, to remove the last traces of hydrochloric acid.

Purification of Oxalic Acid.

29. The commercial oxalic acid contains oxalates. Place 50 c.cs. of hydrochloric acid in a porcelain dish, dilute with water, heat, and add 100 grs. of oxalic acid in small portions, stirring all the time till the solution is saturated. Allow to settle while kept warm on the steam-bath. Pour off the clear liquid and cool rapidly. Filter, wash with *cold* water, redissolve, filter if necessary and allow to crystallise slowly. Drain the crystals at the pump and dry in a desiccator.

PREPARATION OF THE GASES REQUIRED IN SUBSEQUENT EXPERIMENTS.

For the experiments involving the use of a gas, a constant stream will be required. The following methods will be found convenient.

Chlorine.

30. The liquid chlorine now supplied in cylinders by most dealers is a convenient source of the gas when large quantities are required. The gas may be obtained from common salt as follows:

In a flask of $1\frac{1}{2}$ litres capacity fitted with a good cork, safety funnel and delivery tube, place a cold mixture of 110 c.cs. water and 150 c.cs. strong sulphuric acid. To this add an intimate mixture of 120 grams common salt with an equal weight of powdered manganese dioxide. There is no action in the cold, but on warming the mixture on a sand-bath or in a water-bath a slow and continuous stream of chlorine is evolved. The gas should be washed with water to free from hydrochloric acid, and may be dried if necessary by passing through sulphuric acid. (See par. **22.**)

The above quantities will give about 20 litres of chlorine. In cases where measured quantities are required, the student should calculate the amounts to be used.

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

Chlorine may also be obtained readily from a mixture of strong hydrochloric acid and granular manganese dioxide, or coarsely powdered potassium dichromate, heated on wire gauze over a small flame. By regulating the flame the gas may be obtained at the requisite speed.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$
$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Cl_2.$$

For another method see the preparation of sodium hypochlorite (par. **38**).

Hydrogen.

31. A Kipp's generator is charged with commercial granulated zinc, and a mixture of equal volumes of strong hydrochloric acid

and water, or a cold mixture of one volume of strong sulphuric acid with two volumes of water.

The gas liberated by ordinary zinc contains small quantities of arseniuretted hydrogen. This may be obviated to some extent by using platinised or coppered zinc, preferably that free from arsenic and antimony.

The ordinary gas may be purified by washing through potassium permanganate to remove arsenic and antimony (but this introduces slight traces of oxygen), then through caustic soda or potash to remove acids, and finally dried by passing through a sulphuric acid or calcium chloride tube.

Hydrochloric Acid.

32. A Kipp's generator with lumps of rock salt or fused common salt and concentrated sulphuric acid is convenient, and supplies the gas practically pure and dry.

The gas may also be obtained from common salt, using an apparatus similar to that described for the preparation of chlorine. The salt is covered with a cold mixture of sulphuric acid and water in the proportion used for chlorine. No gas is evolved in the cold, but on warming gently a continuous stream of the gas is produced. This may be dried in a sulphuric acid tube, or with calcium chloride.

Ammonia.

33. The gas may be obtained pure by heating a mixture of pure ammonium chloride and lime. For most purposes it may be obtained sufficiently pure by warming the strong aqueous solution in a small flask, and drying in a lime tower (Fig. 25). If much gas is to be prepared a preliminary partial drying may be effected by passing the gas through a small quantity of the strong aqueous solution contained in a wash-bottle cooled by ice and salt.

Carbon Dioxide.

34. Chips of marble, and hydrochloric acid diluted with an equal volume of water, form the most convenient source of

the gas. A Kipp's apparatus is usually kept charged and ready for use. The gas should be washed in water to free from hydrochloric acid, and may be dried by passing through sulphuric acid.

Small quantities of the gas may also be made by heating sodium bicarbonate or magnesium carbonate.

Carbon Monoxide.

35. When formic acid or oxalic acid is heated with strong sulphuric acid, carbon monoxide is evolved, in the latter case mixed with an equal volume of carbon dioxide.

$$H.COOH = H_2O + CO.$$
$$(COOH)_2 = H_2O + CO + CO_2.$$

1. In a small distilling flask heat some concentrated sulphuric acid, and allow formic acid to drop slowly in from a tap-funnel.

2. From oxalic acid the gas may be obtained by heating 50 grams crystallised oxalic acid with enough strong sulphuric acid to cover it. The carbon dioxide is removed by passing the evolved gases through a strong solution of caustic potash.

3. Potassium ferrocyanide also gives carbon monoxide when heated with strong sulphuric acid.

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O$$
$$= 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO.$$

Cover the powdered ferrocyanide in a small flask with strong sulphuric acid, and heat over wire gauze. The action is easily regulated, and the supply of gas may be stopped by cooling the flask.

The gas should be washed in a strong solution of caustic soda or potash, and may be dried with sulphuric acid or calcium chloride.

Sulphur Dioxide.

36. The liquid sulphur dioxide supplied in syphons is very pure. If this is not available the gas may be conveniently prepared

by dropping concentrated sulphuric acid from a tap-funnel on to a quantity of solid sodium bisulphite or of the commercial bisulphite solution, contained in a bottle or flask. Sulphur dioxide gas is immediately liberated, and may be dried, if necessary, by means of sulphuric acid.

Sulphuretted Hydrogen.

37. Ferrous sulphide is readily decomposed by dilute hydrochloric or sulphuric acid, liberating sulphuretted hydrogen. The gas may be generated in a Kipp's apparatus. Hydrochloric acid (equal volumes of acid and water) is preferable to sulphuric acid, as ferrous chloride is more soluble than the sulphate, and there is therefore less risk of the salt crystallising and blocking the apparatus. The gas should be washed with water to remove hydrochloric acid.

Since sulphide of iron often contains particles of free iron, the gas obtained in this way contains a little hydrogen. For ordinary purposes, however, this is not objectionable.

Many forms of apparatus are employed for the preparation of sulphuretted hydrogen. Any apparatus used for hydrogen or carbonic acid gas, such as a Woulff's bottle with thistle funnel and delivery tube, will also serve for the preparation of sulphuretted hydrogen. When a large quantity of the gas is required, this may be made by using two large bottles connected with each other by means of caoutchouc tubing passing between tubulures at the bottom, one bottle containing sulphide and the other the acid. The acid bottle is raised or lowered when necessary.

In most forms of generator the acid is largely wasted, partly because of the imperfect arrangement for mixing the acid, as in the Kipp's generator, and also because the acid when nearly neutralised ceases to act sufficiently rapidly on the sulphide. It therefore has to be renewed before it is exhausted. To obviate this, the method may be used of dropping the acid slowly on to the sulphide contained in a tall glass tower. Before the liquid reaches the bottom of the column of sulphide the acid is in general almost completely neutralised.

PREPARATION OF VARIOUS COMPOUNDS BY THE DIRECT ACTION OF CHLORINE.

Sodium Hypochlorite.[1]

NaOCl.

38. When chlorine gas is passed into a cold solution of caustic potash or soda, a mixture of chloride and hypochlorite is obtained.

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

The reaction is quantitative, and can be employed to prepare solutions containing definite amounts of the hypochlorite.

The chlorine may be prepared by the action of potassium permanganate on hydrochloric acid.

Weigh out 25 grams potassium permanganate and place in a half litre distilling flask fitted with a tap funnel. Arrange to pass the chlorine gas first through a wash bottle with water to free from hydrochloric acid, and then into a solution of 50 grs. caustic soda in 400 c.cs. water, contained in a bottle surrounded by ice so that the temperature may be kept below 5° C. To the permanganate add slowly 150-170 c.cs. strong hydrochloric acid by means of the tap funnel. The reaction is at first instantaneous, chlorine being evolved, but towards the end the liquid should be heated until all the permanganate is reduced and no more chlorine is obtained.

$$K_2Mn_2O_8 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

The chlorine is completely absorbed by the soda. Now make the solution of hypochlorite up to 500 c.cs.; calculate the quantity of hypochlorite contained therein, and estimate the amount by the method given in par. **275**. If the experiment has been well conducted, practically the theoretical amount will be found.

Potassium Chlorate.

$KClO_3$.

39. Chlorine gas acts differently on hot solutions of caustic alkalies, producing a mixture of chlorate and chloride.

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

[1] Graebe, *Berichte* 35, 2753 (1902).

Dissolve 50 grams caustic potash in 250 c.cs. water in a half-litre beaker, and heat on a sand-bath to 65°-75° C. throughout the experiment. Pass in chlorine gas prepared by one of the methods given, using a little more than the quantities of material which will supply the necessary chlorine. The gas should be washed in water to remove hydrochloric acid, and is introduced into the alkali by means of an inverted funnel just touching the surface of the solution. When the reaction is over, filter the solution if necessary, and evaporate slowly to about 180-170 c.cs. On cooling, potassium chlorate will crystallise, but the chloride will remain in solution. Filter at the pump, wash the crystals twice with small quantities of cold water, and set aside to dry. Concentrate the filtrate further, and examine each crop of crystals for chlorate and chloride. Yield of chlorate, 10-15 grs.

Potassium chlorate crystallises from water in colourless transparent monoclinic tables. These melt at 334° C., and begin to decompose at 352°, evolving oxygen. The salt is largely used for the preparation of oxygen, and generally as an oxidising agent.

Potassium Chloride.

KCl.

40. The later crystalline separations obtained in the above experiment, consisting of chloride and chlorate, may be recrystallised together, and pure chloride obtained. This crystallises in cubes, like sodium chloride. It is largely used for the manufacture of other potassium salts.

Potassium Perchlorate.

$KClO_4$.

41. Place 25 grams of pure potassium chlorate in a porcelain dish, and heat carefully on a sand-bath, stirring constantly until the melted chlorate just begins to solidify. When a small sample of the substance, warmed with hydrochloric acid, gives off little or no chlorine, the reaction is complete.

$$4KClO_3 = 3KClO_4 + KCl.$$
$$2KClO_3 = KClO_4 + KCl + O_2.$$

Allow to cool, grind the mass in a mortar with a little water to remove most of the chloride, pour off this liquid and warm the residue with a little hydrochloric acid to decompose any unchanged chlorate. Filter at the pump, wash with a little cold water, and crystallise the residue of perchlorate from hot water. The salt separates in small rhombic crystals. Yield, 10-12 grs.

When heated the perchlorate decomposes into oxygen and potassium chloride.

Anhydrous Ferric Chloride.

$FeCl_3$.

42. A piece of combustion tube about 10 inches long is fitted at each end with a cork carrying a tube, so that dry chlorine gas may be passed through, the excess being absorbed in caustic soda. A porcelain boat is filled with iron filings free from grease (by washing with benzene if necessary), and inserted in the combustion tube near to the end at which the chlorine enters. The iron is heated to dull redness in the stream of dry gas, and anhydrous ferric chloride sublimes on to the cool part of the tube and is there deposited in dark brown hexagonal plates, which have a metallic lustre and appear red by transmitted light. The crystals are deliquescent and easily soluble in water, alcohol and ether. They should be transferred to a tube and sealed up.

Aluminium Chloride.[1]

$AlCl_3$.

43. Arrange an apparatus similar to that used for ferric chloride, but use a longer combustion tube, and heat in a small furnace (Fig. 26). The tube is charged with clippings of aluminium foil, and the chloride, which is very hygroscopic, should be sublimed directly into a dry bottle, into which the end of the combustion tube is inserted through a gas-tight cork, and from which the excess of chlorine is conducted to an absorber.

[1] Gattermann, *Practical Methods of Organic Chemistry*.

Pure aluminium chloride forms colourless hexagonal crystals. The commercial product is often yellow, owing to admixture of ferric chloride. The chloride absorbs water vapour, and is

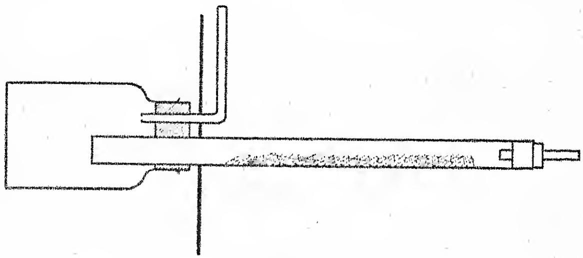


Fig. 26.

soluble in alcohol and ether. It may also be obtained by strongly heating a mixture of alumina and carbon in chlorine gas, as described below for chromium chloride.

Chromic Chloride.

$CrCl_3$.

44. Use the same apparatus as for aluminium chloride, but without the bottle as receiver. Grind up 5-10 grams of chromium sesquioxide and an equal weight of starch into a thick paste with a little cold water. Mould this into balls of the size of peas, dry these carefully and heat on an iron tray until the starch is completely charred. Transfer to the combustion tube, and heat to redness in the stream of dry chlorine. Chromic chloride is obtained in beautiful violet scales, almost insoluble in cold water.

Stannic Chloride.

$SnCl_4$.

45. In a wide glass tube about a foot long and closed at one end, fit an upright condenser and a delivery tube. Fill the wide tube with granulated tin, and pass in dry chlorine gas. The delivery tube should reach at first to the bottom, and should be withdrawn as the liquid tin chloride forms, so that the end just

dips into the liquid. When nearly all the tin is converted into chloride, pour the liquid into a dry distilling flask and collect the portion boiling at 118-122° C.

Tin tetrachloride is a colourless, mobile liquid, fuming in air. Sp. gr. 2·234 at 15°. B. Pt. 120° C. It forms several hydrates with water, of which the crystalline pentahydrate, $SnCl_4 . 5H_2O$, is used as a mordant in dyeing.

Phosphorus Trichloride.

PCl_3.

46. Place 10 grams amorphous phosphorus in a small retort. Insert the stem through a good cork into a distilling flask as receiver, and on the side tube of this, place a small calcium chloride tube. From this lead a tube to an absorber for the excess of chlorine.

Pass dry chlorine gas over the phosphorus, and heat this gently on a sand-bath. If any solid pentachloride is formed, raise the delivery tube further from the phosphorus. The receiver should be kept cool in a vessel of water. Redistil the trichloride, keeping out moisture in a similar manner.

Phosphorus trichloride forms a colourless, fuming liquid; spec. grav. 1·613 at 0° C. B. Pt. 76° C. The vapour is very irritating and poisonous.

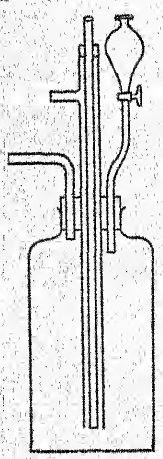


Fig. 27.

Phosphorus Pentachloride.[1]

PCl_5.

47. Fit up an apparatus like that shown in Fig. 27. Through the upper delivery tube dry chlorine is admitted, the excess leaving by the lower tube, which is protected from moisture by a calcium chloride tube. Phosphorus trichloride is introduced, a few cubic centimetres at a time, from the tap-funnel, and when the pentachloride formed appears quite dry,

[1] Gattermann, *Practical Methods of Organic Chemistry*.

the reaction is over. Thus any desired quantity may be prepared; the chlorine delivery tube is raised to keep clear of the pentachloride, and if necessary it may be cleared by means of the glass rod provided. Preserve in the same bottle, well stoppered. Yield, quantitative.

Sulphur Monochloride.

S_2Cl_2.

48. The apparatus used for preparing phosphorus trichloride may also be used for this substance. In the retort place 20 grams dry sulphur, lead in dry chlorine and heat the sulphur gently. It melts and the monochloride distils as a light brown oily liquid. The receiver must be well cooled. The chloride may be purified by redistilling, excluding moisture.

Sulphur monochloride forms a clear, amber-coloured liquid, of specific gravity 1·7 and boiling at 138° C.

Sulphuryl Chloride.

SO_2Cl_2.

49. In a two-necked bottle place 20 grams of camphor, stand the bottle in cold water, and lead in dry sulphur dioxide gas so long as it is absorbed. The camphor liquefies. Now pass in dry chlorine until it is no longer absorbed, then sulphur dioxide, and so on until the volume of liquid no longer increases. Transfer to a dry distilling flask, and collect the fraction below 100°. Purify by redistillation. The higher boiling portion may be used again to prepare more.

Sulphuryl chloride is a colourless liquid, boiling at 70° C. It fumes strongly in air, and is decomposed by water into sulphuric and hydrochloric acids.

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

PREPARATION OF CHLORIDES BY MEANS OF HYDROCHLORIC ACID.

50. Chlorides may be prepared by one or more of the following methods.

(*a*) Direct union of chlorine with the element.

(*b*) Action of hydrochloric acid on the metal.

(*c*) Action of hydrochloric acid on the oxide, hydroxide or carbonate of the metal.

Examples of the first method have already been given. The other methods are applicable to the salts of any metal and may be used with other acids than hydrochloric.

Anhydrous Ferrous Chloride.

$FeCl_2$.

51. In a bulb tube of combustion glass or a piece of combustion tubing 10-12" long place a few grams of clean iron filings. Pass dry hydrochloric acid through the tube, and when air is expelled, heat the iron filings. The vapour of ferrous chloride condenses on the cooler parts of the tube in colourless, six-sided, shining scales, and by suitable heating may be obtained free from the iron and scraped from the tube. The product should be immediately placed in a dry test tube which should then be sealed by softening and drawing out.

$$Fe + 2HCl = FeCl_2 + H_2.$$

Stannous Chloride.

(Tin Salt.)

$SnCl_2 . 2H_2O$.

52. Dissolve 25 grams of granulated tin in 50 c.cs. strong hydrochloric acid, diluted with 25 c.cs. of water, in a $\frac{1}{2}$ litre flask, allow the solution to settle, and decant from any residue into an Erlenmeyer flask. Close this with a cork, and set aside to crystallise. The hydrated salt crystallises in transparent monoclinic prisms, which melt in their water of crystallisation at 40° C., and lose all the water in a vacuum over sulphuric acid. Yield, 35-40 grs.

Stannous chloride is a powerful reducing agent, combining with either chlorine or oxygen. When the solution is exposed to air, or diluted with much water, a basic chloride of the composition $2Sn(OH)Cl . H_2O$ is deposited.

Zinc Chloride.

$ZnCl_2$.

53. This may be obtained by neutralising hydrochloric acid with zinc, or its oxide or carbonate. The solution so obtained is evaporated until the temperature reaches 240° C. Care must be taken that none of the substance comes in contact with the hands. Allow to cool, break into lumps and bottle immediately, making the stopper air-tight with paraffin.

Zinc chloride forms a white, deliquescent mass. It is used in the laboratory as a dehydrating agent, in surgery as a caustic, and in the textile trade for weighting cotton goods. It is also used as an antiseptic, as a preservative for timber, and in wool dyeing.

Cupric Chloride.

$CuCl_2 . 2H_2O$.

54. Use pure copper oxide, prepared by dissolving copper in nitric acid, crystallising and heating the nitrate until decomposition to oxide is complete. Warm the oxide with dilute hydrochloric acid, using the oxide in slight excess. Filter and allow to crystallise. Rhombic prisms or needles of the above composition separate on standing. These are deliquescent, and are soluble in alcohol.

Cuprous Chloride.

$CuCl$.

55. (*a*) A small quantity may be prepared as follows: In a test tube place a few copper turnings, cover with strong hydrochloric acid, add one or two drops of strong nitric acid and boil for five minutes. Pour the liquid into water. The cuprous chloride is precipitated as a white powder.

(*b*) Copper oxide may be substituted for nitric acid.

Place in a ¼-litre flask 20 grs. of copper and 26 grams of copper oxide and add 90 c.cs. of strong hydrochloric acid. Connect with an upright condenser and boil for two hours. Pour all the contents into water, filter quickly, using suction, and wash the precipitate with sulphurous acid, followed by glacial acetic acid.

Heat the product in a porcelain dish on the water-bath till no smell of acetic acid can be detected. Keep in a stoppered bottle.

$$Cu + CuO + 2HCl = 2CuCl + H_2O.$$

(*c*) Heat a solution of 50 grs. copper sulphate and 24 grs. of common salt to 60-70° C. Pass sulphur dioxide through the solution till no further precipitate of cuprous chloride is obtained. Filter, wash and dry as before.

$$2CuSO_4 + 6NaCl + 2H_2O + SO_2 = 2CuCl + 3Na_2SO_4 + 4HCl.$$

Cuprous chloride is insoluble in water, but soluble in hydrochloric acid and ammonia. These solutions are used for the absorption of carbon monoxide. Acetylene is also absorbed by the ammoniacal solution.

Calcium Chloride.

$CaCl_2$.

56. Use the solution of calcium chloride from the carbon dioxide generator. Neutralise the liquid by boiling with a small amount of milk of lime. This will precipitate any iron present. Allow to settle, pour off the clear liquid as far as possible, and filter the remainder. Evaporate until a portion taken on a glass rod rapidly solidifies. To make the product porous, add a few c.cs. of strong hydrochloric acid. Dry by heating in an iron pan, but do not allow the substance to fuse.

Calcium chloride is extremely hygroscopic, and is largely used as a desiccating agent. It combines with ammonia, forming the compound $CaCl_2 . 8NH_3$, and cannot therefore be used for drying ammonia.

Crystallised calcium chloride, $CaCl_2 . 6H_2O$, may be obtained by *slowly* evaporating a concentrated solution obtained as above.

Barium Chloride.

$BaCl_2 . 2H_2O$.

57. (*a*) **From Witherite.** Place 100 grams powdered witherite in a large porcelain dish and mix to a paste with 100 c.cs. water. Add slowly, with constant stirring, a mixture of 75 c.cs. strong hydrochloric acid and 100 c.cs. water. Heat finally

on the steam-bath and stir well till all effervescence ceases. Now add a slight excess of finely powdered witherite and evaporate to dryness. This precipitates iron, calcium, etc., which commonly occur as impurities in the witherite. Extract the residue with half a litre of boiling water, filter, acidify the filtrate with hydrochloric acid, evaporate to half its bulk and allow to crystallise. Concentrate the mother liquor until no more crystals can be obtained and then recrystallise the whole from distilled water. Yield, about 100 grams.

$$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2.$$

(*b*) **From Heavy Spar.** Mix 50 grams finely powdered barytes (or precipitated barium sulphate) with 10 grams powdered charcoal and heat to bright redness in a covered clay crucible in the muffle furnace for 1-2 hours. When cold, extract the mass with boiling water, filter and add hydrochloric acid to the filtrate till the barium sulphide is all decomposed. Crystallise and purify the barium chloride as above. Yield, about 35 grams.

$$BaSO_4 + 4C = BaS + 4CO.$$
$$BaS + 2HCl = BaCl_2 + H_2S.$$

COMPOUNDS OF BROMINE AND IODINE.

Hydrobromic Acid.

HBr.

58. (*a*) In a flask fitted with tap funnel and delivery tube place 5 grs. amorphous phosphorus and 15-20 c.cs. water. Allow 10 c.cs. (30 grs.) of bromine to drop slowly from the funnel. Hydrobromic acid is produced:

$$5Br + P + 4H_2O = H_3PO_4 + 5HBr.$$

To free the gas from bromine, conduct it through a U-tube containing moist asbestos dusted with red phosphorus, and then absorb the gas in 100 c.cs. of water by means of an inverted funnel or retort, or a large pipette, just dipping into the liquid. Distil the acid and collect the constant boiling liquid (123-129°).

(*b*) Pass sulphuretted hydrogen through a mixture of bromine and water until the bromine is decolourised. Remove the excess of hydrogen sulphide with a current of air, filter from

sulphur and distil as above. Some sulphuric acid is also produced.

$$H_2S + Br_2 = 2HBr + S.$$
$$H_2S + 4Br_2 + 4H_2O = 8HBr + H_2SO_4.$$

(*c*) Carry out a similar experiment with sulphur dioxide gas. Leave a little free bromine, or add more bromine water until a slight yellow colour is obtained: remove the excess of bromine with air, and distil.

$$SO_2 + Br_2 + 2H_2O = 2HBr + H_2SO_4.$$

Potassium Bromide.

KBr.

59. (*a*) Place 20 grs. fine iron filings and 200 c.cs. water in a flask, and add slowly 30 grs. (10 c.cs.) bromine, shaking well after each addition. Bromides of iron are produced. To the liquid add now a solution of 25 grs. potassium carbonate so long as a precipitate is formed. Heat nearly to boiling, filter from the excess of iron and precipitated carbonate of iron, and evaporate the liquid. Potassium bromide crystallises in cubes with a saline taste. It is easily soluble in water, and is used in medicine as a sedative. Yield, about 35 grams.

(*b*) By the action of bromine on caustic potash, mixtures of bromide, hypobromite and bromate are obtained, according to temperature and concentration of the liquid (compare chlorine). If the liquid be evaporated to dryness and the residue gently ignited, pure potassium bromide is obtained. This may be redissolved and crystallised.

(*c*) Potassium or sodium bromide may also be obtained by neutralising waste hydrobromic acid solution (obtained in brominating benzene, etc.) with potassium or sodium carbonate, after removing free bromine with a stream of air. The dry residue left on evaporation may be used for the preparation of ethyl bromide, etc.

Potassium Bromate.

$KBrO_3$.

60. To a solution of 40 grs. caustic potash in 200 c.cs. of water, kept at a temperature of 70-80° in a water-bath, add carefully

drop by drop 15 c.cs. (45 grs.) of bromine. Transfer the liquid to a crystallising dish and set aside to cool. Potassium bromate separates, the bromide remaining in solution.

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

It may be recrystallised from hot water, and separates in hexagonal crystals, sparingly soluble in cold water.

Potassium Iodide.

KI.

61. This salt may be prepared by the methods given for potassium bromide, but it is best prepared by the action of iodine on caustic potash and ignition of the dry residue. It crystallises in cubes, very soluble in water and having a sharp, saline taste.

Hydriodic Acid.

HI.

62. (*a*) This acid may be obtained from iodine, red phosphorus and water, as for hydrobromic acid. Place 5 grs. red phosphorus and 20 grs. iodine in the flask, and add water slowly from the dropping funnel until the mixture is covered. Heat finally on the sand-bath to complete the reaction.

(*b*) Pass sulphuretted hydrogen through a mixture of 20 grams powdered iodine and 200 c.cs. water. After a few minutes, when air is expelled from the flask, close the outlet tube, and allow the mixture to stand in contact with sulphuretted hydrogen, with frequent shaking, until all the iodine is dissolved. Remove excess of sulphuretted hydrogen with a stream of air, filter from sulphur, and distil in a current of hydrogen to prevent dissociation of the hydriodic acid. The strongest acid obtained by distillation at ordinary pressures boils at 127°C, and contains 57·7 per cent. of the acid. Collect from 125°-130°C.

(*c*) The acid may be obtained by the direct union of hydrogen and iodine. A hard glass bulb tube is packed with platinised asbestos, prepared by soaking asbestos in a solution of platinic chloride and igniting the dried fibre. Into one end of the tube is inserted the side tube of a small distilling flask containing

iodine, while the other end is connected with a U-tube filled with dry asbestos, from which a glass tube leads to the absorption flask containing water. Pure dry hydrogen is passed through the apparatus; the bulb of platinised asbestos is heated

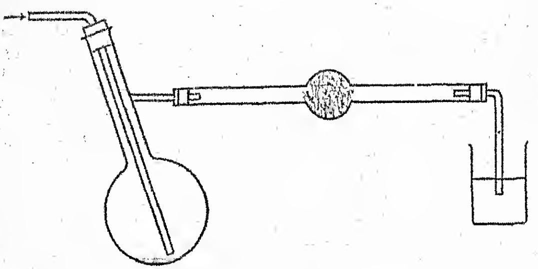


Fig. 28.

to dull redness, while the distilling flask is gently warmed. A mixture of hydrogen and iodine vapour is thus carried over the platinised asbestos; hydriodic acid is produced and the uncombined iodine is deposited in the U-tube.

Iodic Acid.

HIO_3.

63. Place 10 grams iodine in a 250 c.c. round flask, add 100 c.cs. fuming nitric acid, and warm gently until all the iodine is dissolved. Add more nitric acid if required. Nitric oxide is evolved.

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

Evaporate to dryness and heat the residue to 200° to remove all trace of nitric acid. Iodine pentoxide remains as a white powder. Redissolve this in a small quantity of water, and allow to evaporate, when iodic acid will separate in colourless rhombic crystals. It is easily soluble in water, and is reduced by sulphur dioxide, sulphuretted hydrogen, hydriodic acid, etc., with separation of iodine.

PREPARATION OF METALLIC OXIDES.

Cuprous Oxide.

Cu_2O.

64. (*a*) Mix together 20 grams cuprous chloride and 15 grams dry sodium carbonate, and heat gently in a covered crucible. Cuprous oxide is obtained as a non-crystalline red powder.

$$Cu_2Cl_2 + Na_2CO_3 = Cu_2O + 2NaCl + CO_2.$$

Extract the residue when cold with water, to remove sodium chloride and excess of sodium carbonate, filter, wash till free from chloride, and dry the residue of cuprous oxide.

(*b*) Dissolve 20 grams crystallised copper sulphate and 15 grams grape sugar in 200-250 c.cs. water, and add excess of sodium hydrate. Heat gently on a sand-bath, with frequent shaking, until the copper is completely precipitated as cuprous oxide, and the liquid no longer has a blue colour. Allow the precipitate to settle, pour off the clear liquid, and add hot water to the residue. Wash in this way by decantation several times, and then filter and complete the washing on the filter till free from alkali.

Cuprous oxide dissolves in strong hydrochloric acid to form cuprous chloride. It is converted by nitric acid into cupric nitrate, with evolution of nitrogen oxides, and by sulphuric acid into a mixture of cupric sulphate and metallic copper.

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

Manganous Oxalate.

MnC_2O_4;

and

Manganous Oxide.

MnO.

65. Dissolve separately in as little hot water as possible 20 grs. manganous sulphate and 12 grs. ammonium oxalate. Filter the two solutions if they are not quite clear, and mix together. Manganous oxalate is precipitated as a pale pink, crystalline powder. Drain on the pump, wash with a very little cold water, and dry on a porous plate. Place this dry powder in a piece of

hard glass tube 8-12 inches long, pass a stream of dry carbon dioxide gas, and heat gently with the burner until the oxalate is completely decomposed. Manganous oxide remains as a grey-green powder,

$$MnC_2O_4 = MnO + CO + CO_2,$$

which, on exposure to air, changes to higher oxides. Transfer it, while the carbon dioxide is still passing, to a strong tube closed at one end and then seal the tube.

Mercuric Oxide.

HgO.

66. Dissolve mercury in nitric acid and evaporate to dryness. Mix the residue with about an equal weight of mercury, and heat in the porcelain dish, in the fume chamber. The temperature should not be more than sufficient to decompose the nitrate. Use a glass rod to stir the mixture, and break up the pieces of mercuric nitrate. If the temperature is too high, much of the mercury will volatilise, and some of the mercuric oxide will be decomposed. Allow the residue to cool, add water and boil. Filter and wash with hot water to remove undecomposed nitrate. Dry and press through wash leather to remove unaltered mercury. The residue is red.

Mercuric oxide may also be prepared by adding a solution of sodium hydrate to a solution of a mercuric salt. The precipitate is mercuric oxide, and is yellow. It must be *well* washed with hot water to remove the caustic soda. The residue may be dried in an air oven.

Nickel Sesquioxide.

Ni_2O_3.

67. Dissolve 10 grams of pure metallic nickel in dilute nitric acid, make up the solution to 250 c.cs. with distilled water, and filter from any residue. Evaporate to dryness on the steam-bath. Nickel nitrate remains as a green crystalline residue. Transfer to a weighed porcelain dish. [If pure metal is not available, take 50 grams of pure nickel nitrate, free from cobalt, in a weighed porcelain dish.]

Ignite the nitrate, gently at first, to expel all water of crystallisation, in which the salt melts, and then strongly until no further change occurs, and the weight of the residue is constant. Abundant red fumes are evolved, and the green nitrate changes to the dark grey oxide.

The oxide dissolves in nitric or sulphuric acid evolving oxygen, and in hydrochloric acid with evolution of chlorine, and nickelous salts are produced. It is readily reduced, by heating to 200-300° in hydrogen, forming metallic nickel.

Many other oxides may be prepared by this method, as CuO, PbO, BaO, etc.

Chromium Sesquioxide.

Cr_2O_3.

68. Dissolve 20 grams chromium sulphate in 50 c.cs. distilled water, or use the chrome alum obtained in the preparation of aldehyde (par. **120**), heat and add dilute ammonia solution until no more precipitate is obtained. Boil for 15 minutes and allow the precipitate to settle. Decant the clear liquid and wash the precipitate by decantation with boiling water until free from ammonium sulphate. Filter on a fluted filter, and dry in the steam oven. Transfer to a crucible or dish and ignite to convert the hydrate to oxide, then grind to powder in a mortar. A dull green amorphous powder is left, almost insoluble in acids.

Chromium Hydrate.
Guignet's Green.

$Cr_2O(OH)_4$.

69. Mix together 30 grams finely-powdered potassium dichromate and 30 grams crystallised boric acid, and enough water to make a thick paste. Place in fire-clay crucibles and heat to a low red heat. On cooling, extract the fused mass with water and boil to remove boric acid. The residue is a fine green powder, insoluble in water and acids, and is used as a green pigment. Yield, 15-18 grams.

Lead Peroxide.

PbO_2.

70. (*a*)[1] Dissolve 50 grams crystallised lead acetate in 200 c.cs. water in a large flask or porcelain dish and heat on the steam pan. Grind up 100 grams good bleaching powder with water, make up to 1,500 c.cs., shake well, and allow to settle. Filter the cleared solution and add it slowly to the hot solution of lead acetate, with constant stirring or shaking, until a filtered test portion gives no more brown precipitate on boiling with more of the bleaching powder. Continue heating for some time until the precipitated lead peroxide is dark brown in colour. Wash by decantation with hot water until the washings are free from chloride, drain on the pump and dry in the steam oven, or keep the peroxide as a paste under water. Yield, 25-30 grams.

(*b*) Mix 60 c.cs. strong nitric acid with 250 c.cs. water in a porcelain dish, warm gently on the steam-bath, and slowly stir in 70 grams red lead made into a paste with water. Two-thirds of the lead dissolves as nitrate, and lead peroxide remains.

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

Heat on the steam-bath, stirring frequently, for half an hour; allow to settle, decant and wash by decantation as above till no lead can be detected in the washings. Yield, 20-22 grams.

From the filtered solution lead nitrate may be crystallised on cooling.

REDUCTION OF METALLIC OXIDES.

Copper.

71. Fill a porcelain boat with copper oxide. Place it in a piece of combustion tube with a stopper at each end carrying a delivery tube. Pass through the tube a current of hydrogen, taking care to test the gas before heating the tube. The heated oxide is rapidly reduced. Allow to cool in the current of hydrogen.

$$CuO + H_2 = Cu + H_2O.$$

[1] Gattermann, *Practical Methods of Organic Chemistry.*

Coal gas may be substituted for hydrogen, and by finding the weight of oxide used and of copper produced, and repeating the experiment with cuprous oxide, the results obtained may be used to verify the law of multiple proportions.

The law of constant proportions may also be verified by finding the weight of oxide produced when a known weight of reduced copper is heated in air, and dissolving the same weight of copper in nitric acid, evaporating to dryness, decomposing the nitrate by heat and weighing the residue of copper oxide.

Lead.

72. The lead may be obtained as in the last method, or as follows. Heat 6 or 7 grams of an oxide of lead in a carbon crucible in a muffle furnace till reduced.

When cool the bead of lead may be taken out, cleaned from adhering particles of the crucible, and weighed. By repeating with other oxides of lead, the law of multiple proportions may be verified.

Manganese.

73. When certain metallic oxides are heated with aluminium powder, the metal is produced and aluminium oxide formed. The heat produced by the action is so great that it is only necessary to start the action at one point in the mixture. If sufficient material be used, the product will liquefy and a mass of the metal will be obtained.

Prepare about 80 grs. of trimanganese tetroxide by strongly heating the dioxide.

$$3MnO_2 = Mn_3O_4 + O_2.$$

Mix the product with the calculated quantity of aluminium powder and pack tightly in a fireclay crucible. To start the action cover with a thin layer of potassium permanganate and aluminium in equal parts, place a short piece of magnesium ribbon in the centre and light the magnesium. The crucible should be surrounded with sand and as soon as the action is started the lid should be placed on the crucible and more sand put round.

$$8Al + 3Mn_3O_4 = 4Al_2O_3 + 9Mn.$$

When cool break the crucible to obtain the mass of manganese.

Make a similar experiment with chromium sesquioxide.

A mixture of ferric oxide and aluminium powder, which is sold under the name of "Thermit" is used for the production of molten iron at a high temperature.

Sodium Bicarbonate.

$NaHCO_3$.

74. Dilute 250 c.cs. of ·880 ammonia with twice its volume of water and place it in a litre flask. Pass in a steady stream of carbon dioxide till absorption ceases. Keep the flask cool during the operation. If a precipitate forms, add water to dissolve it. Make a saturated solution of 200 grs. of common salt in water and add to it the solution of ammonium bicarbonate till no further precipitation is observed. Keep the solution cool during the addition. Filter, wash the precipitate with small amounts of cold water to remove the ammonium chloride, and dry in a steam oven.

$$NH_3 + H_2O + CO_2 = NH_4HCO_3.$$
$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

Compare this method with the Solvay or Ammonia Soda process.

The solubility of sodium bicarbonate is 9·8 at 20°C., that of the normal carbonate being 21·4.

Sodium carbonate may be prepared from the bicarbonate by heating or by boiling the aqueous solution :

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Sodium Carbonate.

$Na_2CO_3 . 10H_2O$.

(Washing Soda.)

75. Heat 500 c.cs. of water to boiling in a beaker and add in small portions about 200 grs. of soda ash. If the solution is yellow add a small quantity of bleaching powder. Filter through a cloth filter, concentrate and allow to cool. Press the crystals between filter paper and dry in the air till efflorescence commences. Store in a well-stoppered bottle.

To obtain free from sulphates and chlorides commence with sodium bicarbonate. Place in a funnel plugged with cotton wool and wash repeatedly with small quantities of distilled water. Test the filtrate for chlorides and sulphates. When free from these, place the bicarbonate in a platinum dish and dry in the air oven. Heat strongly till the weight is constant. The product contains small traces of silica. Dissolve it in hot water and crystallise.

Sodium carbonate crystallises in large monosymmetric crystals containing 10 molecules of water of crystallisation. The crystals are efflorescent, forming $Na_2CO_3 . H_2O$. The student should notice the solubility curve for the crystals.

Sodium Hydrate.
NaOH.

76. In a large beaker place some water and boil. Add in portions 50 grs. of sodium carbonate (anhydrous) or 100 grs. washing soda and when dissolved add about 50 grs. of slaked lime. Boil, filter 2 or 3 drops and test with acid. If no effervescence occurs the action is complete. Allow to settle, decant the clear liquid and evaporate.

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

Sodium Hydrate.
(By Electrolysis.)

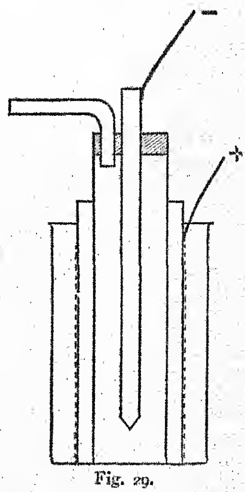


Fig. 29.

77. Take a large beaker and place in it a large porous cell round which is placed a piece of wire gauze to act as a cathode. Inside the porous cell place a cylindrical lamp chimney fitted with a 2-holed rubber stopper. Through one hole place a carbon rod to act as anode and through the other an exit tube for the chlorine produced. Coat the rubber stopper with paraffin.

Pour into the porous pot and beaker a saturated solution of common salt in water. The porous pot prevents the chlorine produced during electrolysis from acting on the sodium hydrate. The most suitable current will depend upon the dimensions of the different portions of the apparatus, and the student should carefully note the nature of the current used. All phenomena should be entered in the notes, and should include the sp. gr. of the electrolytes before and after electrolysis, and of the sodium hydrate obtained. The chlorine may be absorbed by slaked lime to form bleaching powder.

Sodium Sulphite.

$Na_2SO_3 . 7H_2O$.

78. Dissolve 30 grams crystallised sodium carbonate in 100 c.cs. of water, and divide the solution into two equal parts. Saturate one half with sulphur dioxide. Carbon dioxide is expelled and sodium bisulphite produced.

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

Now add the other half of the sodium carbonate solution. More carbon dioxide gas is evolved, and sodium sulphite formed.

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + CO_2 + H_2O.$$

The normal sulphite crystallises from this solution in transparent monoclinic prisms. The crystals are efflorescent, and lose the whole of the water of crystallisation at 150° C. The solution has an alkaline reaction.

Sodium Hydrogen Sulphite.

$NaHSO_3$.

79. This salt may be obtained from the above solution saturated with sulphur dioxide in the cold. It can be crystallised by allowing the solution to evaporate slowly in the cold, and is precipitated from the aqueous solution in the form of a white powder, by the addition of alcohol. It has an acid reaction, smells of sulphur dioxide, and liberates the gas on heating or on boiling the aqueous solution, leaving the normal sulphite.

Sodium Thiosulphate.

$Na_2S_2O_3 . 5H_2O.$

80. Prepare sodium sulphite as above from 25 grams sodium carbonate, or dissolve 25 grs. sodium sulphite in 100 c.cs. water, and add 5 grs. flowers of sulphur. Boil gently for about half an hour until the alkaline reaction of the sulphite has disappeared, and filter. Sodium thiosulphate is produced by the union of sulphur with the sulphite,

$$Na_2SO_3 + S = Na_2S_2O_3,$$

and crystallises from the filtrate in large transparent monoclinic prisms, containing five molecules of water.

It is also prepared by passing sulphur dioxide into a solution of sodium sulphide.

The salt is unchanged by exposure to air, and the aqueous solution is neutral. The crystals melt in their own water at 45° C., and lose all the water at 215°C. On further heating the substance decomposes with liberation of sulphur. When the solution is acidified with hydrochloric acid, no immediate change is apparent, but the unstable thiosulphuric acid is liberated, which gradually decomposes, liberating sulphur and sulphur dioxide.

$$H_2S_2O_3 = H_2O + SO_2 + S.$$

Iodine solution is at once decolourised, and thiosulphate is largely used for the estimation of free iodine and as an antichlor in the bleaching of paper pulp, calico, etc.

$$2Na_2S_2O_3 + I_2 = 2NaI + \underset{\text{Sodium tetrathionate.}}{Na_2S_4O_6}.$$

The solution of thiosulphate also dissolves silver halides, and is employed as a fixing agent in photography, usually under the erroneous name of "hyposulphite."

$$Na_2S_2O_3 + AgCl = NaCl + AgNaS_2O_3.$$

Barium Dithionate.

$BaS_2O_6 . 2H_2O.$

81. 20 grams of finely-powdered manganese dioxide are suspended in water and sulphur dioxide is passed in, with

frequent shaking, until no more of the oxide will dissolve. The solution contains manganese dithionate and a small quantity of sulphate.

$$MnO_2 + 2SO_2 = MnS_2O_6.$$
$$MnO_2 + MnS_2O_6 = 2MnSO_4.$$

The manganese salt may be obtained in easily soluble rhombohedral crystals, with three molecules of water, $MnS_2O_6 . 3H_2O$. It is better to prepare the barium salt, which can be obtained quite free from sulphate by adding a solution of barium hydroxide as long as a precipitate forms.

$$MnSO_4 + Ba(OH)_2 = BaSO_4 + Mn(OH)_2.$$
$$MnS_2O_6 + Ba(OH)_2 = BaS_2O_6 + Mn(OH)_2.$$

Warm gently and filter off the precipitated barium sulphate and manganese hydroxide. Barium dithionate can then be crystallised from the filtrate by slow evaporation in a warm place. It forms colourless, transparent rhombic prisms.

On heating dithionates in a dry tube, or on boiling the aqueous solution for some time, especially in presence of a little hydrochloric acid, they are all decomposed into sulphur dioxide and the sulphate.

$$BaS_2O_6 = BaSO_4 + SO_2.$$

Note for student. Devise a scheme to distinguish between sulphites, bisulphites, thiosulphates, sulphates, and dithionates.

Sulphuric Acid.

H_2SO_4.

82. The manufacture of sulphuric acid by the chamber process may be illustrated with the aid of the following apparatus: A large dry flask or bottle of 2-3 litres capacity is used as the reaction chamber, and into this are passed from separate generators sulphur dioxide, vapour of nitric acid, air, and steam. An exit tube must also be provided for the excess of gas. Fit up the apparatus in the fume chamber, and commence by introducing gradually into the dry flask sulphur dioxide from the generator (par. **36**), in which strong sulphuric acid is dropped into sodium bisulphite solution, and nitric acid from a small

flask containing a mixture of sodium nitrate and strong sulphuric acid. The nitric acid is reduced by sulphur dioxide, forming red fumes of nitrogen peroxide, while sulphuric acid is simultaneously formed.

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2.$$

After a short time also a white crystalline deposit appears on the inside of the flask. This is chamber crystal, or nitrosulphonic acid, and is formed by the action of nitric acid on sulphur dioxide in the absence of water.

$$SO_2 + HNO_3 = O_2S{<}\begin{matrix}OH.\\ O.NO.\end{matrix}$$

This deposit is at once decomposed on the admission of steam, forming sulphuric and nitrous acids,

$$SO_2 . OH . NO_2 + H_2O = H_2SO_4 + HNO_2,$$

the latter decomposing with effervescence into water, nitric oxide and peroxide.

$$2HNO_2 = H_2O + NO + NO_2.$$

The nitrogen peroxide produced above also plays an important part in the oxidation of sulphur dioxide, being reduced to nitric oxide,

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO.$$

and this nitric oxide again combines with oxygen from the air introduced, thus acting as a "carrier" of oxygen to the sulphur dioxide. For this reason a small quantity only of nitric acid is required, provided the oxides of nitrogen are retained in the chamber. Hence the use of the Glover and Gay Lussac towers in the technical process.

When the above operations have been continued for about an hour, air being introduced from time to time from the gasholder, a considerable quantity of dilute sulphuric acid will have collected. The liquid will be strongly acid, and will decompose sodium carbonate and dissolve zinc or iron, liberating hydrogen. It will also give a white precipitate with barium chloride, insoluble in acids.

Evaporate one-fourth or less of the liquid in the fume cupboard, until white fumes begin to be evolved. The residue is now strong sulphuric acid, a heavy oily liquid. After cooling,

pour into a little cold water in a test tube and note the evolution of heat. It may now be added to the main portion of the liquid, the whole boiled to expel oxides of nitrogen, and then converted into the following salts.

Magnesium Sulphate.

$MgSO_4 . 7H_2O$.

(Epsom Salt.)

83. Neutralise one half of the dilute sulphuric acid obtained above with magnesium carbonate, heat nearly to boiling and filter at once. Magnesium sulphate crystallises from the filtrate in four-sided rhombic prisms containing seven molecules of water of crystallisation. When heated, the crystals melt in this water, and lose six molecules at 150°, the seventh at 200°. The crystals are isomorphous with the corresponding sulphates of zinc, iron, nickel, etc.

Epsom salt is used in medicine as a purgative, and is also employed in dressing and weighting cotton goods, and as a mordant in dyeing.

Copper Sulphate.

$CuSO_4 . 5H_2O$.

(Blue Vitriol.)

84. The other half of the dilute sulphuric acid solution is neutralised by boiling with copper oxide, or by adding copper carbonate. The blue filtered solution deposits copper sulphate on cooling, in transparent, blue triclinic crystals containing five molecules of water. Four of these are lost at 100°, the fifth at 220-230°. Copper sulphate is used as a mordant in calico-printing, and in dyeing, in making certain pigments, as Scheele's green and emerald green, and in the electrometallurgy of copper.

Purification of Copper Sulphate.

85. The commercial copper sulphate contains some iron. Dissolve 200 grams in 300 c.cs. of hot water, add 12 grams of lead peroxide and boil for an hour, keeping a constant bulk of liquid by addition of water. Add barium carbonate and stir well, keeping the solution warm.

Test a few c.cs. as follows. Filter, add ammonium hydrate in excess and filter again. Wash the filter paper, and if a brown precipitate is seen iron is present.

Oxidise the original substance further with lead peroxide, add more barium carbonate if necessary and again test. If free from iron filter the whole of the liquid, concentrate and crystallise.

Zinc Sulphate.

$ZnSO_4 . 7H_2O$.

(White Vitriol.)

86. The solution from the hydrogen generator may be used, excess of zinc being added to render the solution as nearly neutral as possible and to prevent the solution of arsenic and lead which may be present as impurities. Filter the supernatant liquid through an asbestos filter. Oxidise any iron present by passing chlorine through the solution. The iron should not be precipitated with ammonium hydrate owing to the formation of ammonium sulphate which will crystallise with the zinc sulphate. It may be precipitated by boiling with a small quantity of zinc carbonate (which may be prepared by precipitating a small portion of the solution with sodium carbonate, filtering and washing the precipitate), stirring during the heating.

Test the clear liquid with potassium sulphocyanide for iron, and if free, filter through asbestos and evaporate the filtrate till saturated. Allow the solution to crystallise. Press the crystals between filter paper and dry at a low temperature.

Zinc sulphate crystallises in long rhombic prisms which are efflorescent. At 100° C. it parts with 6 molecules of water of crystallisation, and with the last molecule at 300° C. It decomposes on heating strongly, forming zinc oxide. It is used in medicine and in dyeing and printing.

Potassium Dichromate.

$K_2Cr_2O_7$.

87. Take 30 grams of finely powdered chromite, or chromium sesquioxide, Cr_2O_3, and mix well by grinding in a mortar with 30 grams powdered potassium nitrate and 20 grams dry potassium carbonate. Place the mixture in a large earthenware crucible

and heat to redness in a muffle furnace for several hours. Allow to cool and extract the yellow mass with boiling water. Filter from oxide of iron and concentrate the solution.

$$Cr_2O_3 . FeO + 4K_2O + 7O = 4K_2CrO_4 + Fe_2O_3.$$

Add sulphuric acid till the solution is strongly acid. The chromate is converted into dichromate, which crystallises readily. Filter the crystals at the pump, using a plug of asbestos or glass wool instead of paper, wash with a little cold water, and concentrate the filtrate. The later separations are liable to contain potassium sulphate. Recrystallise the dichromate from hot water. It crystallises in orange-red triclinic prisms, without water of crystallisation. These melt without decomposition below a red heat, and decompose at higher temperature into oxygen, chromium sesquioxide and the normal potassium chromate.

Potassium dichromate is largely used in dyeing and calico-printing, as an oxidising agent, and in the preparation of other chromium compounds. The solution has an acid reaction, and is poisonous.

Potassium Chromate.

K_2CrO_4.

88. Dissolve 30 grams potassium dichromate in 100 c.cs. water, and add slowly to the warm solution 14 grams dry potassium carbonate. The normal chromate is produced:

$$K_2Cr_2O_7 + K_2CO_3 = 2K_2CrO_4 + CO_2.$$

Boil the liquid to expel carbon dioxide, filter and evaporate. The salt crystallises in yellow rhombic pyramids and is very soluble in water, but insoluble in alcohol. The solution has a strong yellow colour, and an alkaline reaction. When heated the salt becomes darker in colour and melts at a high temperature without decomposition.

Chromium Trioxide.

CrO_3.

(Chromic Anhydride.)

89. Dissolve 60 grams of potassium dichromate in 100 c.cs. water, and add 85 c.cs. strong sulphuric acid. Allow the

mixture to stand overnight in a cool place, when potassium bisulphate will crystallise out. Decant the liquid, heat the mother liquor to 80-90° C., and add 30 c.cs. strong sulphuric acid. If a precipitate of chromium trioxide separates, add water till it just redissolves. Evaporate on the steam until crystals begin to form in the liquid, and set aside for a day. Decant the liquor and evaporate to obtain a further crop. Drain the crystals on a funnel loosely plugged with glass wool, using the pump, and wash twice with small quantities of strong nitric acid to remove sulphuric acid and sulphates. Place in a porcelain dish and dry by heating very gently on a sand-bath.

Chromium trioxide crystallises in long rhombic prisms of a deep crimson colour. It melts unchanged at 195°, forming a deep-red liquid, and at 250° decomposes into oxygen and the sesquioxide. It is a powerful oxidising agent.

Lead Chromate.

$PbCrO_4$.

(Chrome Yellow.)

90. Dissolve 100 grs. of lead acetate or lead nitrate in water. Calculate the necessary quantity of potassium dichromate or potassium chromate and dissolve in water. Filter the solutions, mix the clear liquids and stir well. Wash the precipitate well by decantation, testing the supernatant liquid for lead and chromate. When free from these pour off the liquid and filter through a fluted filter or cloth filter. Press out as much water as possible, break up and dry in the steam oven.

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2KNO_3 + 2HNO_3.$$

The precipitate is chrome yellow and may be obtained in lighter shades by replacing a portion of the potassium dichromate with sodium sulphate, when lead sulphate will be precipitated with the chromate.

Chrome Red.

Take a portion of the yellow precipitate before drying and boil with dilute caustic soda solution. The yellow colour will

change to orange or red owing to the formation of basic chromate of lead.

$$2PbCrO_4 + 2NaOH = PbCrO_4 . PbO + Na_2CrO_4 + H_2O.$$

These chromates are used as pigments.

Potassium Permanganate.
$KMnO_4$.

91. Place 70 grams caustic potash and 30 grams potassium chlorate in a deep iron sand tray, add 50 c.cs. water and warm until all is dissolved. Stir in 60 grams finely-powdered pyrolusite, and evaporate with constant stirring until the paste solidifies. Cover with another dish and heat to dull redness until the mass is quite hard and dry. Allow to cool, break up and powder the dark green or brown mass of potassium manganate, and boil in $1\frac{1}{2}$ litres of water for an hour, while passing a stream of carbon dioxide gas. A heavy precipitate of manganese dioxide is formed. Continue this until the liquid is violet in colour. The manganate is now changed to permanganate.

$$3MnO_2 + KClO_3 + 6KOH = 3K_2MnO_4 + KCl + 3H_2O.$$
$$3K_2MnO_4 + 2CO_2 = K_2Mn_2O_8 + 2K_2CO_3 + MnO_2.$$

Allow the precipitate to settle, decant through a glass-wool filter, wash the precipitate twice with boiling water, and concentrate the combined filtrates. Allow to cool in a covered dish and avoid all contact with dust, organic matter, or reducing gases.

Potassium permanganate crystallises in dark violet rhombic prisms, with a green metallic lustre. The crystals are isomorphous with potassium perchlorate. Heated alone, they decompose into oxygen, manganese dioxide, and potassium manganate which is also further decomposed. The substance is largely used as an oxidising agent in the laboratory, and as a disinfectant (Condy's fluid).

Ammonium Nitrate.
NH_4NO_3.

92. In a 6-inch porcelain dish place 100 c.cs. of strong nitric acid and dilute with twice its volume of water. Add ammonium

hydrate (1 pt. of ·880 ammonia to 2 pts. of water) till the solution after stirring smells slightly of ammonia. Evaporate the liquid till a portion taken on the end of a glass rod rapidly solidifies. Allow to cool, and when solid, warm the dish to loosen the substance, and remove it from the dish. Break up into small pieces and use for the preparation of nitrous oxide.

If, during the neutralisation, a brown sediment is produced (probably traces of iron and tarry matter from the ammonia), allow to settle and filter.

To obtain crystals, evaporate the solution till saturated and allow to cool. Dry the crystals between filter papers.

$$NH_3 + HNO_3 = NH_4NO_3.$$

Sodium Nitrite.

$NaNO_2$.

93. Place 20 grs. of sodium nitrate in a tin dish and melt over a bunsen flame. Add 60 grs. of lead parings and continue heating and stirring till nearly all the lead is converted to litharge. Allow to cool, lixiviate and allow the clear liquid to crystallise.

$$NaNO_3 + Pb = NaNO_2 + PbO.$$

Sodium nitrite crystallises in deliquescent prisms and is largely used in the preparation of dye stuffs.

Estimate the nitrite by potassium permanganate (see par. 257).

Lead Nitrate.

$Pb(NO_3)_2$.

94. Wash the residue (litharge) obtained in the last experiment with hot water. Place it in an evaporating dish and add water, stir and add nitric acid in small portions till all the litharge is dissolved, keeping the solution hot during the experiment, and the bulk of liquid constant by addition of water. Evaporate to dryness on the water-bath. Dissolve in water, filter, add a few c.cs. of nitric acid, evaporate till concentrated and allow to crystallise.

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Lead nitrate crystallises in regular octahedra, and has a solubility of 50 at ordinary temperatures.

Hydroxylamine Sulphate.

$(NH_2OH)_2 . H_2SO_4$.[1]

95. Dissolve 75 grams sodium nitrite and 140 grams crystallised sodium carbonate in as little ice water as possible, and pass in sulphur dioxide until the solution is just acid, stirring well and keeping the liquid at 2-3° below zero by immersion in ice and brine. The nitrite is completely converted at this temperature into sodium oximidosulphonate.

$$NaNO_2 + Na_2CO_3 + 3SO_2 + H_2O = HO . N(SO_3Na)_2 + NaHSO_3 + CO_2.$$

Add a few drops of sulphuric acid; the temperature rises, owing to hydrolysis of the oximidosulphonate into oxamidosulphonate.

$$HO . N(SO_3Na)_2 + H_2O = HO . NH(SO_3Na) + NaHSO_4.$$

Heat slowly to 90°, and keep the solution at 90-95° for two days, to complete the hydrolysis into hydroxylamine sulphate.

$$HO . NH(SO_3Na) + H_2O = NH_2 . OH + NaHSO_4.$$

The liquid must not be boiled, or much of the hydroxylamine will be destroyed. To ascertain whether the change is complete, add excess of barium chloride to a small portion of the liquid, filter, and boil the filtrate with a crystal of potassium chlorate, to convert any sulphonate into sulphate. If no further precipitate is obtained, the hydrolysis is complete.

Now neutralise the solution with sodium carbonate, using methyl orange as indicator, and evaporate till the liquid weighs 790-820 grams. Cool to 0° or − 5°, when nearly all the sodium sulphate will crystallise out. Filter, wash the crushed crystals with a little ice-water, and evaporate until the liquor, on cooling to the room temperature, gives a large quantity of hydroxylamine sulphate. Evaporate the mother liquor carefully, separate sodium sulphate as before, and then obtain more hydroxylamine sulphate. Purify the latter by recrystallisation. Yield of crude hydroxylamine sulphate, about 60 grams.

The salt forms large, non-deliquescent crystals, soluble in three-quarters of its weight of water at 20° C. The free base is

[1] Divers and Haga, *Trans. Chem. Soc.* (1896), 1665.

alkaline in reaction, and is a strong reducing agent, precipitating gold and mercury from their solutions, and cuprous oxide from cupric salts.

Copper Acetate.

$(CH_3COO)_2Cu . H_2O.$

96. To a solution of copper sulphate, made by dissolving 20 grs. of the salt in water, add sodium carbonate to precipitate the copper as basic carbonate. Filter by suction, wash well, transfer to a porcelain dish, and warm with acetic acid till dissolved. The acid should be diluted before use, and added in slight excess. Evaporate till concentrated and allow to crystallise.

$$CuCO_3 + 2CH_3COOH = (CH_3COO)_2Cu + H_2O + CO_2.$$
$$Cu(OH)_2 + 2CH_3COOH = (CH_3COO)_2Cu + 2H_2O.$$

Copper acetate is used as a mordant, chiefly in the form of verdigris, a basic copper acetate approximately of the formula $2Cu(C_2H_3O_2)_2 . CuO$, but of varying composition. This is also used as a green pigment, but is not good, the colour being altered by moisture and light.

Antimony Trichloride.

$SbCl_3.$

97. Place 50 c.cs. of concentrated hydrochloric acid in a porcelain dish and add in small portions 30 grs of antimony trioxide, stirring during the addition. Heat gently and then boil till excess of acid is driven off and a drop of the liquid solidifies on cooling. Transfer to a retort fitted with a thermometer, and distil. When the temperature reaches 200° C. collect the antimony trichloride in a dry receiver.

$$Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O.$$

Antimony trichloride is a deliquescent white crystalline substance, melting at 72° and boiling at 223°. It decomposes in water, but dissolves in alcohol unchanged. It is known as "butter of antimony." It may be crystallised from carbon disulphide.

Silicic Acid and Pure Silica.

98. In a dry half litre flask fitted with thistle funnel and delivery tube place a mixture of 20 grs. of fine sand and 25 grs. of powdered fluor spar. Allow the delivery tube to dip just below the surface of mercury (about 1 in. deep) contained in a gas jar. Have the delivery tube perfectly dry. Pour water (6 in. deep) on the surface of the mercury. Down the thistle funnel pour strong sulphuric acid and shake the flask to moisten the whole mass. (If any of the mixture at the bottom of the flask remains dry, the flask will probably crack on heating.) Heat the flask on a sand-bath. Silicon tetrafluoride is given off, and bubbling through the mercury is decomposed by the water, forming a precipitate of silicic acid and leaving in solution hydrofluosilicic acid. Filter, dry the precipitate and heat strongly. Pure silica is left. The filtrate may be used for the preparation of barium fluosilicate.

$$2CaF_2 + 2H_2SO_4 = 2CaSO_4 + 4HF,$$
$$4HF + SiO_2 = SiF_4 + 2H_2O,$$
$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6,$$
$$H_4SiO_4 = 2H_2O + SiO_2.$$

Ammonium Sulphide.

$(NH_4)_2S$.

99. Take 50 c.cs. of ·880 ammonia and dilute to 200 c.cs. Divide into two equal parts. Saturate one with sulphuretted hydrogen and add it to the other.

$$NH_4OH + H_2S = NH_4SH + H_2O,$$
$$NH_4SH + NH_4OH = (NH_4)_2S + H_2O.$$

Ammonium sulphide is used as a reagent, but for this purpose it is generally best prepared by adding ammonium hydrate to the solution to be tested and passing a few bubbles of hydrogen sulphide through the mixture.

Ammonium sulphide decomposes on standing, liberating ammonia and sulphur, the latter dissolving in undecomposed ammonium sulphide, forming a yellow solution.

Yellow Ammonium Sulphide.

$(NH_4)_2S_{1+x}$.

100. Pour the colourless solution of ammonium sulphide, as prepared above, over sulphur standing in a filter paper placed in a funnel. The sulphur dissolves, forming polysulphides of ammonium.

$$(NH_4)_2S + xS = (NH_4)_2S_{1+x}.$$

The polysulphides are decomposed by acids and sulphur is precipitated;

$$(NH_4)_2S_{1+x} + 2HCl = 2NH_4Cl + H_2S + xS.$$

Yellow ammonium sulphide is used as a solvent to remove the sulphides of arsenic, antimony and tin from those of the other metals of the copper group.

Cadmium Sulphide.

CdS.

(Cadmium Yellow.)

101. Dissolve 10 grs. of cadmium sulphate or chloride in water and pass sulphuretted hydrogen through the solution. Wash the precipitate well and dry in the steam oven.

$$CdSO_4 + H_2S = CdS + H_2SO_4.$$

Cadmium sulphide has a pure yellow colour and is not precipitated in strongly acid solutions. Owing to the liberation of acid during precipitation a further precipitate may be obtained on dilution of the filtrate.

Cadmium sulphide is used as a yellow pigment (cadmium yellow). The colour is permanent, unlike that of chrome yellow (lead chromate) which is blackened by sulphuretted hydrogen. The colour becomes deeper, approaching orange, as the strength of the acid is increased in the solution in which the sulphide is precipitated.

Phosphoric Acid.

H_3PO_4.

102. Place 10 grams of red phosphorus in a porcelain dish, cover with water and add concentrated nitric acid of equal bulk. Place in the fume cupboard and warm gently. Copious red

fumes will be evolved. When the action moderates add nitric acid, if necessary, in small quantities till all oxidation ceases. Heat to drive off excess of nitric acid, dilute the syrupy liquid with water, filter and evaporate till the temperature reaches 200° C. About 25 grs. of syrup of sp. gr. 1·85 will be obtained.

Sodium Phosphates.

103. Phosphoric acid is tribasic, and forms three distinct classes of salts, which may be obtained as follows.

DISODIUM HYDROGEN PHOSPHATE.

Take some syrupy phosphoric acid, dilute with water and divide into three equal parts.

To one part add sodium hydrate solution till a drop taken on the end of a glass rod is just alkaline to litmus. The solution now contains disodium hydrogen phosphate. Crystallise.

The amount of sodium hydrate solution required for neutralisation should be noted.

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O.$$

MONOSODIUM HYDROGEN PHOSPHATE.

To a second part of the phosphoric acid solution add half the quantity of sodium hydrate solution used in the last preparation, and crystallise.

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O.$$

TRISODIUM PHOSPHATE.

To the third part add three times the quantity of sodium hydrate used in the last preparation, and crystallise the normal phosphate.

$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O.$$

The disodium phosphate is the common phosphate of soda, and crystallises in large monoclinic prisms which contain 12 molecules of water of crystallisation and are efflorescent.

The monosodium phosphate forms large rhombic crystals, containing 4 molecules of water of crystallisation, and having an acid reaction.

The normal phosphate crystallises in thin six-sided prisms containing 12 molecules of water of crystallisation. Its solution in water is strongly alkaline.

When heated the first yields sodium pyrophosphate,

$$Na_2HPO_4 = Na_4P_2O_7 + H_2O,$$

and the second, at 204° sodium hydrogen pyrophosphate,

$$2NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O.$$

At 240° this loses the remainder of its water, yielding sodium metaphosphate.

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

Microcosmic Salt.

(Salt of Phosphorus), $Na(NH_4)HPO_4 . 4H_2O$.

104. Calculate molecular proportions of sodium phosphate crystals and ammonium chloride to make 100 grams of the mixture. Dissolve the sodium phosphate by adding in portions to 100 c.cs. of boiling water in a flask which should be shaken during solution. Add the ammonium chloride, dissolve, filter if necessary and allow to crystallise. By fractional crystallisation free the substance from sodium chloride.

$$Na_2HPO_4 + NH_4Cl = Na(NH_4)HPO_4 + NaCl.$$

Microcosmic salt (sodium hydrogen ammonium phosphate) crystallises with 4 molecules of water. It is efflorescent and when heated leaves sodium metaphosphate. The fused metaphosphate unites with metallic oxides, forming orthophosphates, some of which are coloured, and is therefore used as a dry test for metals.

$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O,$$

$$NaPO_3 + CuO = \underset{\text{(blue bead)}}{CuNaPO_4}.$$

Silica is insoluble in a metaphosphate bead.

Arsenic Acid.

$AsO(OH)_3$.

105. In a half-litre retort place 50 grams arsenious oxide in small lumps, and 50 c.cs. strong nitric acid. Direct the retort neck upwards to act as a reflux condenser, and connect the end by means of a glass tube with a small flask immersed in ice water, in which the nitrous fumes may be condensed. Heat

the retort gently on a sand-bath until no more fumes are evolved. Pour off the liquid, evaporate to dryness and test the residue for arsenious acid. If present add aqua regia and again evaporate to dryness until free from arsenious acid. Dissolve in hot water and again evaporate to dryness to expel nitric acid. The residue can then be crystallised from a little hot water. It

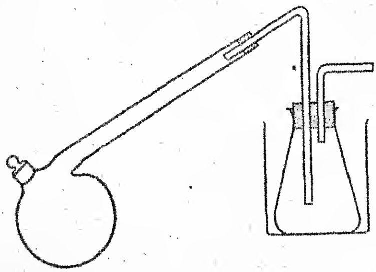


Fig. 30.

forms transparent crystals having the formula $2H_3AsO_4 . H_2O$. These melt at 100°, giving off the crystal water, and leaving a white crystalline powder of orthoarsenic acid, H_3AsO_4.

Examine the dark-blue liquid which has condensed in the small flask. It contains nitrogen trioxide and tetroxide. Pour it into cold water, and test the solution for nitrous and nitric acids.

Sodium Arsenate.

$Na_2HAsO_4 . 12H_2O$.

106. (*a*) To the arsenic acid obtained in last experiment add a slight excess of sodium carbonate; filter, and evaporate the solution at a temperature not exceeding 18° C. The crystals obtained have the above composition, are isomorphous with sodium phosphate, $Na_2HPO_4 . 12H_2O$, and efflorescent. At 20° and higher temperatures the crystals contain only seven molecules of water, and are not efflorescent.

(*b*) Place 20 grams of white arsenic in a porcelain dish, add water, and sodium carbonate solution in slight excess. When all is dissolved add a solution of 15 grams sodium nitrate,

evaporate to dryness and ignite in a clay crucible. Dissolve the residue in water, filter and crystallise as above.

Sodium arsenate is readily soluble in water, and the solution has a feeble alkaline reaction. It is used in dyeing alizarines, and in calico-printing.

Silver Nitrate.

(From Silver Residues.)

107. Add strong hydrochloric acid to the residues, allow to settle, pour off the clear liquid, filter, wash well and dry. Mix the dry residue with four times its weight of fusion mixture together with half its weight of potassium nitrate and place in a fireclay crucible. Heat strongly in a furnace, pour on to an iron plate and allow to cool. Remove as much carbonate from the button as possible by scraping, and boil the silver with hydrochloric acid to dissolve any remaining carbonate.

Dissolve the silver in nitric acid diluted with half its volume of water. Evaporate to dryness to remove nitric acid, dissolve in distilled water, filter and allow to crystallise.

Silver nitrate forms large colourless rhombic plates which melt at 218° C. and resolidify on cooling to a white fibrous mass known as lunar caustic. Silver nitrate is used largely in analytical and photographic work, and is also employed in medicine and for marking inks.

Platinic Chloride.[1]

(From Scrap Platinum), $PtCl_4$.

108. Scrap platinum, which may contain iridium, osmium, etc., is dissolved in aqua regia, and the solution evaporated to dryness; the residue is dissolved in moderately strong hydrochloric acid, and again evaporated to dryness. The dry chloride is now dissolved in hot water containing some hydrochloric acid, and a large excess of caustic soda added. The liquid is boiled for some time to reduce the higher chlorides of metals other than platinum, the latter remaining in the platinic condition,

[1] Thorpe, *Quant. Chem. Anal.*, Appendix.

and a few drops of alcohol are added to destroy any sodium hypochlorite that may be formed. The precipitate is redissolved in hydrochloric acid, the liquid filtered if necessary, and a hot, saturated solution of ammonium chloride is added so long as a precipitate forms. This precipitate consists of ammonium platinum chloride, and should be bright yellow in colour. It is washed by decantation, dried, and gently heated in a current of dry hydrogen. The reduced metal should then be weighed, dissolved in aqua regia, the solution evaporated to expel nitric acid, and then made up to a definite volume. The strength of this solution is thus approximately known.

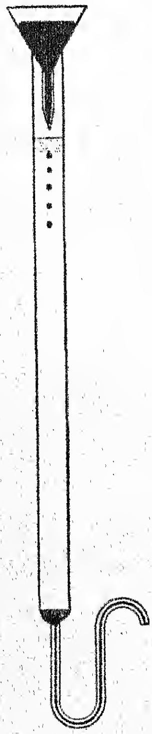


Fig. 31.

Purification of Mercury.

109. Allow the mercury to fall in a succession of small drops from the end of a funnel through a long column of dilute nitric acid of spec. grav. 1·1 (15 per cent. HNO_3, made by mixing 1 part of strong acid with three of water). Syphon off the acid, wash the mercury several times with water, syphoning off the water, and then dry the mercury, first with blotting paper, finally on the steam pan.

A mercury purification tube may also be used (Fig. 31). The bottom is first filled with pure dry mercury, nitric acid is introduced, and the stream of impure mercury started. The process is then automatic, the purified mercury syphoning over into a receiver, in which it may be dried by placing in the steam oven.

The best method for the purification of mercury is that of distillation, which may be carried out in a glass retort. Pure mercury boils at 357° C.

B. CARBON COMPOUNDS.

Methane.

(Marsh Gas), CH_4.

110. This gas may be obtained by heating anhydrous sodium acetate with caustic alkalies.

$$Na \,.\, C_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$

Mix together 10 grs. of freshly-fused sodium acetate and 30 grs. of granulated soda-lime, which has been previously heated and allowed to cool in the desiccator. Place the mixture in a hard glass test-tube or flask, heat carefully, and collect the gas over water. About 2 litres of gas will be evolved.

Show that bromine water and potassium permanganate are not affected by the gas, by adding these reagents respectively to two jars of the gas and shaking well. The gas is therefore saturated. With a third jar show that lime-water is not affected; then burn the gas, noting the appearance of the flame, and show that carbon dioxide is produced.

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Potassium Ethyl Sulphate.

$C_2H_5 \,.\, K \,.\, SO_4$.

111. 60 c.cs. of alcohol and 25 c.cs. strong sulphuric acid are mixed carefully in a half-litre round flask. Much heat is developed, and ethyl hydrogen sulphate is formed.

$$C_2H_5OH + H_2SO_4 \rightleftarrows C_2H_5 \,.\, H \,.\, SO_4 + H_2O.$$

As this reaction is reversible, it is incomplete unless a large excess of either alcohol or sulphuric acid be used. As the removal of much sulphuric acid from the product would be troublesome, excess of alcohol is employed, the above quantity being twice that theoretically required for 25 c.cs. of acid. Heat the flask for 3 hours in a boiling water-bath under a reflux condenser. The mixture now contains much ethyl hydrogen sulphate and water, together with some free sulphuric acid and

alcohol. Cool the flask under the tap, and pour the liquid into cold water in a large flask or dish. Neutralise with chalk or barium carbonate. This precipitates insoluble calcium or barium sulphate, while the calcium or barium ethyl sulphate is left in solution. Filter and evaporate to crystallising point. Colourless crystals of the salt

$$(C_2H_5 . SO_4)_2Ca . 2H_2O \text{ or } (C_2H_5 . SO_4)_2Ba . 2H_2O$$

are obtained.

To prepare the potassium salt from these, dissolve in water and add carefully to this solution, or to the mother liquor, a dilute solution of potassium carbonate, until no further precipitate of calcium or barium carbonate is produced. On evaporating the filtered liquid colourless tables of the anhydrous potassium salt, $C_2H_5 . K . SO_4$, are obtained.

REACTIONS. 1. Heat a few crystals of the potassium salt in a dry test-tube. The salt melts and then decomposes, giving off ethylene gas, which can be ignited at the mouth of the test-tube, and leaving a residue of potassium bisulphate.

$$C_2H_5KSO_4 \rightarrow C_2H_4 + KHSO_4.$$

2. Dissolve a crystal of the potassium salt in water; add a little dilute hydrochloric acid and barium chloride. There is no precipitate. Boil for a few minutes. A white precipitate of barium sulphate is gradually formed, as ethyl sulphuric acid is hydrolysed by boiling water.

$$C_2H_5HSO_4 + H_2O \rightarrow C_2H_5OH + H_2SO_4.$$

Ethylene.

(Olefiant Gas), C_2H_4.

112. The most convenient method is the action of sulphuric acid on alcohol.

30 c.cs. alcohol are placed in a ½-litre flask, and 80 c.cs. concentrated sulphuric acid carefully mixed with it. Some sand may be added to diminish frothing during the experiment. The flask is fitted with a thistle-funnel or tap-funnel passing below the surface of the liquid, and a delivery tube. The gas should be washed by passing through one or two wash-bottles containing caustic soda solution, and collected over water.

The mixture is carefully heated on a sand-bath, the flame being turned low as soon as gas begins to be evolved, at about 140° C. To continue the supply of gas, a mixture of equal volumes of strong sulphuric acid and alcohol may be added slowly from the tap-funnel.

$$C_2H_5OH + H_2SO_4 = C_2H_5 . HSO_4 + H_2O.$$
$$C_2H_5 . HSO_4 = C_2H_4 + H_2SO_4.$$

Collect several jars of the gas and show that it decolourises bromine and potassium permanganate; the gas is unsaturated. Show that it has no action on lime-water, but forms carbon dioxide when burned.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

Ethylene Dibromide.

$C_2H_4Br_2$.

113. This may be prepared by absorbing ethylene gas in bromine. After collecting the gas required in last experiment, allow the supply to pass into two glass wash-bottles, the first containing 20 c.cs. (60 grams) and the second 10 c.cs. of bromine, covered with water one inch deep. These wash-bottles should be kept cool in a trough of water. The bromine is gradually decolourised, forming a heavy colourless oil. Transfer this to a separating funnel, separate from the aqueous layer, and wash the oil with caustic soda until all free bromine and hydrobromic and sulphurous acids are removed. The oil should now be colourless. Transfer it to a small Erlenmeyer flask, add some anhydrous sodium sulphate to dry it, cork the flask and allow to stand over night. The oil may then be filtered into a small distilling flask and distilled. B. pt. 131°·5 C., sp. gr. 2·17 at 20° C.

Acetylene.

C_2H_2.

114. (*a*) From ethylene dibromide, by the action of alcoholic potash.

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

In a small flask place half a stick of caustic potash and 10 c.cs. alcohol and shake gently until the potash dissolves.

Then add 2-3 c.cs. ethylene dibromide and warm gently, collecting the evolved acetylene over water. Examine its behaviour with permanganate and bromine water, and on burning.

(*b*) From calcium carbide by the action of water.

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

Place some pieces of carbide in a small distilling flask fitted with tap-funnel. From the latter allow water to drop slowly on to the carbide, when acetylene will be rapidly and continuously evolved. The gas may be collected over water, and its properties examined as above.

(*c*) From cuprous acetylide. See below.

Cuprous Acetylide.

$$C_2Cu_2.$$

Dissolve a little cuprous chloride (par. **55**) contained in a small flask, in a slight excess of ammonium hydrate, and allow acetylene to enter. A dark red-brown precipitate is produced, consisting of cuprous acetylide.

$$Cu_2Cl_2 + C_2H_2 = C_2Cu_2 + 2HCl.$$

This precipitate is stable in water, but is very explosive when dry. Allow the precipitate to settle, and wash by decantation with cold water. Nearly fill the flask with dilute hydrochloric acid, attach a delivery tube, and warm gently. Acetylene is evolved.

$$C_2Cu_2 + 2HCl = C_2H_2 + Cu_2Cl_2.$$

Acetylene Tebrabromide.

$$C_2H_2Br_4.$$

115. Acetylene unites with bromine to form a dibromide and a tetrabromide:

$$C_2H_2 + Br_2 = C_2H_2Br_2\;;\; + Br_2 = C_2H_2Br_4.$$

In the apparatus used for preparing ethylene dibromide, decolourise a similar quantity of bromine with acetylene from calcium carbide, and purify the heavy oily tetrabromide as for the ethylene compound. A colourless liquid is obtained, of sp. gr. at $21{\cdot}5/4 = 2{\cdot}9629$ and b. pt. $114°$ at 12 mm.

Ethyl Alcohol.

$C_2H_5 . OH.$

116. Ordinary alcohol is manufactured from starches, by converting those first into glucose and then fermenting the latter with yeast.

Grape Sugar.

(Glucose) from Starch.

Mix 20 grams of potato starch to a thin cream with cold water, and pour this into about a litre of boiling water contained in a large flask. Transfer about 100 c.cs. to each of two smaller flasks and allow to cool to 30-40° C. To the main portion add 5 c.cs. dilute sulphuric acid and boil gently on a sand-bath until a few drops of the liquid, diluted with water in a test-tube, give no blue (starch) or brown (dextrins) colour with a drop of iodine solution. The starch is then completely hydrolysed into grape sugar.

$$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6.$$

Neutralise the sulphuric acid with chalk, filter and evaporate to dryness on the steam-bath.

To the two smaller portions of starch solution add respectively a little diastase and a little aqueous extract of crushed malt, which contains diastase. Trace the change into grape sugar as above, and then add to the filtered main portion and evaporate.

Reactions. 1. Heated in a dry tube, grape sugar melts readily, gives off water, and then chars, evolving combustible gases with an odour of burnt sugar, and leaving a residue of carbon.

2. Heated with strong sulphuric acid, the mixture turns yellow, then brown, afterwards charring and evolving sulphur dioxide and carbon dioxide.

3. Grape sugar reduces Fehling's solution on warming, giving a red precipitate of cuprous oxide. (Distinction from cane sugar.)

4. Ammoniacal silver is also reduced, giving a silver mirror.

Alcohol.

(From Grape Sugar.)

117. 100 grams of commercial dextrose, or the substance prepared as in last experiment, is placed in a flask or bottle, dissolved in 750 c.cs. water, and 20 grams of yeast, mixed to a uniform cream with water, then added. Fermentation soon sets in, and proceeds most rapidly about 25° C. Attach a delivery tube to the flask and show that the gas evolved is carbon dioxide.

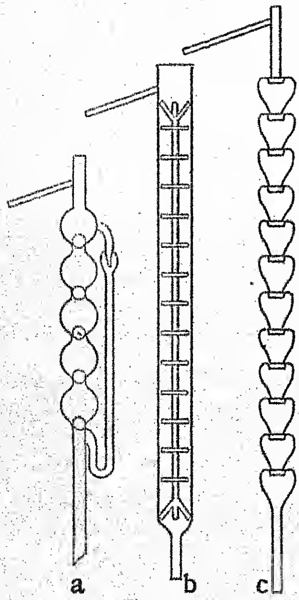


Fig. 32.

$$C_6H_{12}O_6 = 2C_2H_5 . OH + 2CO_2.$$

When the evolution of gas ceases (arrange to leave overnight), distil the filtered liquid, using a Young or Glinsky fractionating column. Collect in the first distillation up to 95° C. About 75 c.cs. of dilute alcohol will be obtained. Redistil this portion and collect up to 85° C. This will give about 50 c.cs. of alcohol, which may be further dehydrated by adding a few pieces of quick lime.

Alcohol is a colourless, pleasant smelling liquid, boiling at 78°·3 C. and of sp. gr. ·793 at 15°. It mixes with water in all proportions, evolving heat.

REACTIONS. 1. Ethyl alcohol burns with a pale, slightly luminous flame.

2. On mixing with strong sulphuric acid, ethyl hydrogen sulphate is formed with evolution of heat. On warming, the mixture gives off inflammable vapours (ethylene, ether, etc.).

3. When warmed with strong sulphuric acid and sodium

acetate, ethyl acetate is formed, recognised by its pleasant fruity smell.

$$C_2H_5 . OH + CH_3 . COOH = CH_3 . CO . OC_2H_5 + H_2O.$$

4. Acetaldehyde is produced on warming ethyl alcohol with potassium dichromate and dilute sulphuric acid, and is easily detected by its smell and its property of reducing ammoniacal silver.

$$C_2H_5 . OH + O = CH_3 . CHO + H_2O.$$

5. To an aqueous solution of alcohol add a little iodine solution and then sodium hydrate until the colour of the iodine is nearly destroyed. A pale yellow crystalline precipitate of iodoform is thrown down. Note the odour (distinction from methyl alcohol).

Ethyl Bromide.

C_2H_5Br.

118. The hydroxyl group in alcohols may be replaced by one atom of a halogen, in various ways. The most convenient method for the preparation of ethyl bromide is to distil a

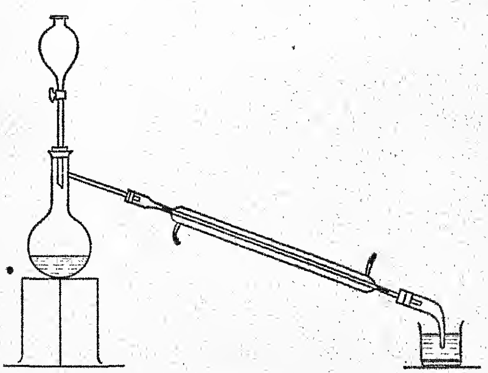


Fig. 33.

mixture of alcohol and potassium or sodium bromide with sulphuric acid.

$$C_2H_5OH + HBr = C_2H_5Br + H_2O.$$

In a half-litre distilling flask (Fig. 33) place 25 grs. (30 c.cs.)

alcohol and 50 grs. (28 c.cs.) strong sulphuric acid. Mix well and cool under the tap. Then add 50 grs. coarsely powdered potassium bromide, and warm gently on a sand-bath. Ethyl bromide distils and is condensed in a long condenser, on the end of which is placed an adapter, which dips just under the surface of water in the receiver. The oily drops of ethyl bromide sink to the bottom of this water, and when no more oil is obtained the operation is finished. Transfer the contents of the receiver to a separating funnel, wash the bromide with dilute sodium carbonate solution, then with water, and place in a dry, well-corked flask with a little anhydrous calcium chloride or sodium sulphate. After standing overnight, or for at least six hours, decant or filter into a small distilling flask and distil over a small naked flame, placing a few chips of porous plate in the liquid. Collect as ethyl bromide the fraction boiling at 35-40° C. Yield 40 grs.

Ethyl bromide is a colourless, ethereal smelling liquid, insoluble in water, but miscible with alcohol and ether in any proportion. B. pt. 38·8° C.; sp. gr. 1·47 at 15° C.

Ethane.

C_2H_6.

(From Ethyl Bromide.)

119. By replacing the atom of bromine by one of hydrogen, the hydrocarbon ethane is obtained.

$$C_2H_5Br + 2H = C_2H_6 + HBr.$$

This may be accomplished by using various reducing agents. In a small flask (100 c.cs., Fig. 34), place a mixture of 20 grs. zinc dust and 2-3 grs. powdered copper oxide. Fit a two-holed stopper to the flask, carrying a long straight calcium chloride tube and a bent tap-funnel. From the upper end of the calcium chloride tube, which is to be filled with coppered zinc, a delivery tube is connected to the collecting trough. The coppered zinc is prepared by placing a sufficient quantity of granulated zinc in a dilute solution of copper sulphate, until it becomes coated with copper, then washing with water and finally with alcohol. The object of this tube of coppered zinc is to remove vapour of ethyl bromide from the ethane.

In the tap-funnel place a mixture of 10 c.cs. of ethyl bromide and 10 c.cs. alcohol, and allow this to drop slowly on to the zinc copper couple in the flask. Ethane is evolved and is collected

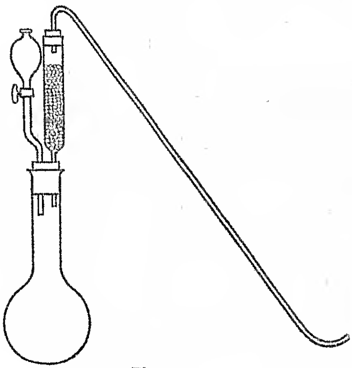


Fig. 34.

over water. Examine its properties as for methane, and compare with those of the hydrocarbons already prepared.

By this method also methane may be prepared from methyl iodide,

$$CH_3I + CH_3OH + Zn = CH_4 + ZnI(OCH_3),$$

ethylene from ethylene dibromide,

$$C_2H_4Br_2 + Zn = C_2H_4 + ZnBr_2.$$

Oxidation of Alcohol.

120. Alcohol may be oxidised by the moderate action of oxidising agents, producing first acetaldehyde and then, by further oxidation, acetic acid.

$$C_2H_5OH + O = CH_3CHO + H_2O,$$
$$CH_3CHO + O = CH_3.COOH.$$

Acetaldehyde.

$CH_3.CHO.$

In a flask of 1·5-2 litres capacity (Fig. 35) place 140 grs. coarsely powdered potassium dichromate and 550 c.cs. water.

The flask is placed on a sand-bath, and is fitted with a tap-funnel and connected with a good condenser and a receiver cooled in ice water. From the funnel introduce a cooled mixture of 148 grs. (190 c.cs.) alcohol and 184 grs. (100 c.cs.) strong sulphuric acid. The dichromate is reduced, as shown by the darkening of colour, and sufficient heat is evolved to cause the aldehyde to distil. When the first reaction subsides, heat the liquid and continue the distillation until all aldehyde has passed over; no smell of aldehyde should then be detected on opening

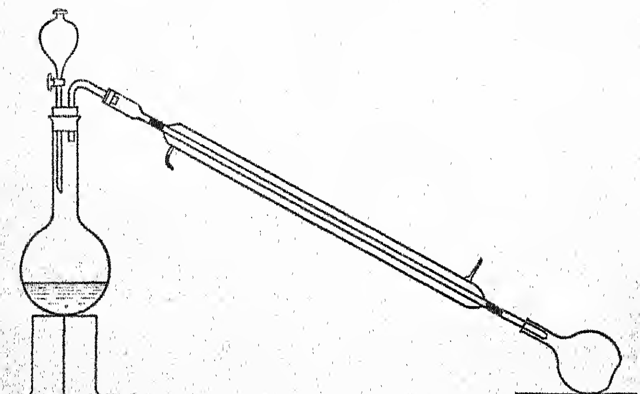


Fig. 35.

the flask, and the distillate should occupy 180-190 c.cs. The residue in the flask may be used to obtain chrome alum.

This distillate is a mixture of aldehyde, alcohol and water, and may be tested for aldehyde as follows:

REACTIONS. 1. Warm with ammoniacal silver solution in a test-tube placed in a beaker of hot water. A mirror of metallic silver is produced.

$$C_2H_4O + Ag_2O = 2Ag + C_2H_4O_2 \text{ (acetic acid).}$$

2. Apply the iodoform test (par. 117, 5). A yellow precipitate of iodoform is produced.

3. Add a few drops to a small quantity of a saturated solution

of sodium bisulphite and shake well. A white, crystalline addition compound, $CH_3CH . OH . SO_3Na$, separates on standing.

Aldehyde Ammonia.

$$CH_3 . CH{<}^{OH}_{NH_2}.$$

121. The aldehyde obtained above may be purified by conversion into aldehyde ammonia.

$$CH_3CHO + NH_3 = CH_3 . CH{<}^{OH}_{NH_2}.$$

To the flask containing the impure aldehyde connect, by means of an adapter or by inclining the flask, a reflux condenser

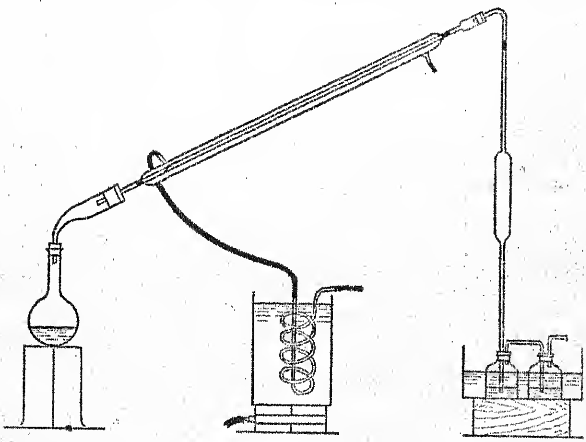


Fig. 36.

(Fig. 36), the upper end of which is connected by a glass tube with a 100 c.c. pipette, which passes nearly to the bottom of the first of two small wash bottles connected in series. These last contain each about 25 c.cs. of ether, and are kept cool by standing in ice water. Through the condenser a stream of water at 30-40° C. flows. Place a few pieces of broken pot in the flask, and boil the liquid gently until all aldehyde has passed

over into the ether. The water and alcohol are condensed and returned to the flask.

Now saturate this ethereal solution of aldehyde with ammonia, by passing the dry gas (see par. **33**, Fig. 25) through the pipette, still keeping the wash bottles in ice water. After a short time colourless crystals of aldehyde ammonia separate. These may be filtered at the pump, washed with a little ether and dried.

To obtain pure aldehyde from this substance, place it in a small flask, cover with a cold mixture of equal volumes of sulphuric acid and water, and distil from a water-bath, collecting the aldehyde in a well-cooled receiver. The distillate may be dehydrated over calcium chloride, and again distilled from this.

Pure aldehyde is a colourless liquid, with a pleasant smell. B. pt. 21° C.; sp. gr. ·807 at 0°. It mixes with water, alcohol and ether in all proportions.

Acetic Acid.

$CH_3 . CO . OH.$

122. In a half-litre round flask connected with an upright condenser place 30 grs. coarsely powdered potassium dichromate and a cold mixture ot 30 grams strong sulphuric acid and 20 c.cs. water. From the top of the condenser introduce slowly a mixture of 10 c.cs. alcohol and 10 c.cs. water, so that the reaction does not become too violent. When all is introduced, boil gently on a sand-bath until the smell of aldehyde is no longer observed on opening the flask. This will require about half an hour. The alcohol is now completely oxidised to acetic acid.

Now rearrange the condenser, and distil until the distillate is only slightly acid. The pure acid is best obtained from its salts. Neutralise the dilute acetic acid with sodium carbonate, filter and crystallise the salt. Sodium acetate forms colourless crystals, containing three molecules of water of crystallisation, $Na . C_2H_3O_2 . 3H_2O$.

To obtain pure acetic acid, the sodium salt may be mixed with concentrated sulphuric acid and distilled. The acid is a colourless liquid, solidifying at low temperatures; m. pt. 16·5°; b. pt. 119°; sp. gr. 1·055 at 15° C. The acid has a pungent

smell, and blisters the skin. The salts are soluble in water, and are decomposed on heating, giving off inflammable vapours (acetone, marsh gas, etc.) and leaving a residue of the metal or its carbonate or oxide.

$$(CH_3COO)_2Ca = CaCO_3 + CH_3 . CO . CH_3 \text{ (acetone)}.$$

REACTIONS. 1. Mix a little sodium acetate in a watch glass with a few drops of strong sulphuric acid, and note the smell of acetic acid.

2. To a little dry sodium acetate or glacial acetic acid in a test tube add a little alcohol and strong sulphuric acid, and warm gently. Ethyl acetate is formed, and is indicated by its pleasant fruity smell.

3. To a neutral solution of an acetate add ferric chloride solution. A red-brown colour, due to ferric acetate, is produced, and on boiling, brown ferric acetate is precipitated.

$$(CH_3COO)_3Fe + 2H_2O = (CH_3COO)Fe(OH)_2 + 2CH_3COOH.$$

Lead Acetate.

(Sugar of Lead.)

123. Dilute 50 c.cs. of glacial acetic acid with 100 c.cs. of water and neutralise with litharge or lead carbonate, warming meanwhile on the water-bath. Filter and evaporate the solution of lead acetate. Colourless crystals are obtained, having the composition $(CH_3CO . O)_2Pb . 3H_2O$.

Ethyl Acetate.

$CH_3 . CO . OC_2H_5$.

124. In a half-litre distilling flask place a mixture of 50 c.cs. alcohol and 50 c.cs. strong sulphuric acid. Fit the flask with a tap-funnel and a thermometer, the latter dipping into the liquid, and with a condenser and receiver. The flask is heated on a sand-bath until the thermometer indicates 140°, and at this temperature a mixture of 100 c.cs. alcohol and 100 c.cs. glacial acetic acid is dropped into the liquid, as rapidly as ethyl acetate distils over. The distillate is a mixture of ethyl acetate, alcohol, water and acetic acid, with sulphurous acid if any charring has occurred. It is washed with sodium carbonate solution in a

separating funnel until neutral, then with calcium chloride solution, and then dried over anhydrous sodium sulphate.

Filter into a dry distilling flask, and distil over a naked flame; some ether passes over first. Collect as ethyl acetate the portion from 74-80°.

Ethyl acetate is a colourless liquid, with a pleasant fruity smell. It mixes with alcohol and ether in all proportions and is soluble in about 11 times its volume of water. B. pt. 77° C.; sp. gr. ·9068 at 15° C.

Hydrolysis of Ethyl Acetate.

125. In a small round flask fitted with upright condenser place 20 c.cs. ethyl acetate and 15 grs. of caustic potash dissolved in 50 c.cs. of water. Boil gently over wire gauze until the upper layer of acetate has disappeared, and no smell of the acetate can be detected. Then distil about 20-25 c.cs. of liquid; this is a mixture of alcohol and water. Add solid potassium carbonate until the alcohol separates as an upper layer, which may then be distilled.

Neutralise a portion of the residue in the flask, and test for acetic acid as above. The ethyl acetate has been hydrolysed or saponified.

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH.$$

Soap.

126. Soaps are the sodium salts (hard soaps) or potassium salts (soft soaps) of the acids occurring in the natural fats and oils, from which they are prepared by the action of the caustic alkalies. Chemically, the process is similar to that used in the last experiment.

Weigh out 100 grs. of beef suet or palm oil, place in a large porcelain dish with half its bulk of water, and warm until melted. Add 20 grams of caustic soda dissolved in 100 c.cs. of water, and boil gently with frequent stirring, or blow steam into the liquid, until the mixture is homogeneous, and all fat has disappeared. Now add 200 c.cs. of a saturated solution of common salt, stir well, and set aside to cool. The soap will

separate as a firm curd on the surface, and may be removed with a spatula.

$$\underset{\text{Glycerin palmitate.}}{(C_{15}H_{31}COO)_3C_3H_5} + 3NaOH = \underset{\text{Sodium palmitate.}}{3C_{15}H_{31}COONa} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3}.$$

Ether.

$(C_2H_5)_2O.$

127. Ethers have structurally the same relation to the alcohols that sodium oxide has to its hydroxide.

$$\begin{matrix}Na\\Na\end{matrix}{>}O\ ;\quad Na-OH\ ;\quad \begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O\ ;\quad C_2H_5-OH.$$

They are prepared by the dehydration of alcohols, usually by means of sulphuric acid ; the alkyl hydrogen sulphate is first formed, and reacts with a second molecule of the alcohol, producing the ether :

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$
$$C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$

The ether and some of the water distil, while sulphuric acid is regenerated. A large quantity of ether may therefore be prepared from a relatively small amount of sulphuric acid.

In a half-litre distilling flask, connected to a long condenser (see preparation of aldehyde, par. **120**), and fitted with a thermometer reaching nearly to the bottom, and a tap-funnel, place a mixture of 120 c.cs. alcohol and 80 c.cs. concentrated sulphuric acid. Heat the flask on a sand-bath to 140°, and keeping the temperature at 140-145°, run in alcohol as fast as the ether distils. This should be collected in a well-cooled receiver, connected to the condenser by means of an adapter. It is advisable also to place a tinplate or cardboard screen across the working bench between the receiver and the burner, as ether vapour is very inflammable.

Collect about half a litre of ether, transfer to a separating funnel and wash with dilute sodium hydrate to remove sulphurous acid. Then wash with a strong solution of calcium chloride or common salt to remove alcohol, and finally transfer the ether to a dry flask and allow to stand over dry calcium chloride. The last traces of water and alcohol can only be

removed with metallic sodium, which has no action on pure ether.

Ether is a colourless, mobile liquid, boiling at 35° C., and of sp. gr. ·720 at 15°. It burns with a luminous flame, is miscible with alcohol, but sparingly soluble in water (9 vols.).

Note. In all operations with ether, the neighbourhood of flames must be avoided.

Chloroform.

$CHCl_3$.

128. 150 grs. of good bleaching powder are triturated in a large mortar with 500-600 c.cs. water, using the water in portions, and the milky liquid is poured into a 2-litre flask. To this liquor add 35 c.cs. alcohol or acetone, connect with a good condenser, and warm gently on a sand-bath. Chloroform and water, with a little alcohol or acetone, distil. When no more can be obtained, dilute the distillate with water to precipitate the chloroform completely, separate in a funnel, and wash with caustic soda, then with water, and dry in a corked flask with dry calcium chloride. Distil the chloroform from a small dry distilling flask.

Chloroform is a colourless, highly-refractive liquid of sp. gr. 1·526 at 0°; b. pt. 61° C. Miscible with alcohol or ether, but only slightly soluble in water. It has a sweet smell, and is a valuable anaesthetic.

Iodoform.

CHI_3.

129. In a quarter-litre flask place 20 grs. crystallised sodium carbonate and 100 c.cs. water and warm on the steam or water-bath. When the carbonate is dissolved, add 10 c.cs. acetone, and then, keeping the temperature at 60-70°, add gradually 10 grs. of powdered iodine. Iodoform separates as a pale yellow crystalline powder. Filter on the pump, wash with cold water, and crystallise from a little acetone.

Iodoform crystallises in thin, yellow, hexagonal plates, melting at 119° C. Insoluble in water; soluble in alcohol, ether, chloroform, etc. It is volatile on heating, and the vapour has

anaesthetic properties. (Note the structural resemblance to chloroform.) It is extensively used in surgery as an antiseptic dressing, and in ointments, and has a peculiar and very persistent odour.

Oxalic Acid.

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} . 2H_2O.$$

130. Oxalic acid is manufactured by oxidation of wood sawdust. It may also be obtained from many carbohydrates by oxidising with nitric acid.

In a large beaker place 100 c.cs. strong nitric acid, and 30 grams powdered cane sugar. Cover with a clock glass and heat gently on a water or steam-bath, in the fume chamber, until the reaction sets in. Abundant red fumes are evolved. When the first violent reaction is over, evaporate in the fume chamber to about 30 c.cs. and allow to cool. Oxalic acid crystallises in long colourless crystals, which should be drained on a small porcelain funnel and recrystallised from a little hot water.

The acid forms colourless crystals, containing two molecules of water of crystallisation. The crystals melt at 101·5°, losing their water, and the anhydrous acid sublimes slowly, melts at 189°, and decomposes at higher temperatures into carbon dioxide and formic acid.

REACTIONS. 1. Heated with a little strong sulphuric acid, oxalic acid decomposes, without charring, into carbonic oxide, carbon dioxide, and water.

$$H_2C_2O_4 = CO + CO_2 + H_2O.$$

2. To a neutral solution of an oxalate add calcium chloride; a white crystalline precipitate of calcium oxalate, CaC_2O_4, is formed, insoluble in ammonia or dilute acetic acid.

3. To a solution of oxalic acid or a salt add dilute sulphuric acid and a little potassium permanganate, and warm gently. The permanganate is reduced and decolourised, and the oxalic acid oxidised to carbon dioxide and water.

$$H_2C_2O_4 + O = 2CO_2 + H_2O.$$

The oxalates of the alkali metals on ignition leave carbonates, those of heavy metals, oxides. Refer to the preparation of manganous oxide, MnO (par. 65).

Methyl Alcohol.

$CH_3 . OH$.

131. This alcohol is obtained in the distillation of wood, and is the chief constituent of wood spirit. The pure alcohol is a mobile colourless liquid ; b. pt. 66-67° : sp. gr. ·796 at 20°. It is miscible with water, and in general properties resembles ordinary alcohol, but it does not give the iodoform reaction. Commercial wood spirit contains a little acetone, which does give iodoform.

REACTIONS. 1. Methyl alcohol is readily oxidised on heating with potassium dichromate and sulphuric acid, giving formaldehyde and formic acid.

$$CH_3OH + O = H . CHO + H_2O.$$
$$H . CHO + O = H . COOH.$$

The formic acid may be distilled and detected as under.

2. To a little methyl alcohol add some salicylic acid and strong sulphuric acid and warm gently. Methyl salicylate (oil of wintergreen) is produced.

Formic Acid.

$H . CO . OH$.

132. The acid may be obtained by oxidising methyl alcohol, but is most conveniently prepared from oxalic acid, by decomposing it in presence of glycerol, which prevents the further decomposition of the formic acid.

$$H_2C_2O_4 = H . COOH + CO_2.$$

In a large retort place 100 c.cs. glycerol and 50 grs. crystallised oxalic acid. Attach a condenser, and fit a thermometer in the retort, with the bulb dipping into the liquid. Heat on a sand-bath. At 90° carbon dioxide begins to be evolved, and at 100-110° water and formic acid distil. When the temperature reaches 110° allow to cool to about 80°, add another 50 grs. of

oxalic acid and distil as before to 110°. Repeat until 150-200 grs. oxalic acid have been used. The residue in the retort still contains some glyceryl formate. It should be transferred to a large flask, and distilled with steam until the distillate is no longer acid. The distillate consists of an aqueous solution of formic acid. It may be converted into

Lead Formate.

$Pb(HCO.O)_2$.

133. Neutralise the heated liquid by stirring in lead carbonate until the addition of more produces no further effervescence. Filter, wash the residue, and evaporate the filtrate. The lead formate crystallises in long colourless needles.

Pure formic acid may be obtained by heating the dry lead salt to 100° in a stream of dry sulphuretted hydrogen,

$$Pb(HCOO)_2 + H_2S = PbS + 2H.COOH,$$

or by distilling the dilute acid until the constant boiling hydrate ($4CH_2O_2 + 3H_2O$) is obtained, boiling at 107·1° at 760 mm. This contains 77 per cent. of formic acid. Dissolve in this, anhydrous oxalic acid, which on crystallising will remove the water. The liquid remaining is now almost pure formic acid, and may be distilled again.

Properties. A colourless, mobile liquid, m. pt. 8·6° C., b. pt. 100·6° C., sp. gr. 1·22 at 20°. It mixes with water and alcohols in all proportions, has a pungent, acid smell, and raises blisters on the skin.

REACTIONS. 1. Heated with concentrated sulphuric acid, formic acid or formates decompose into carbon monoxide and water.

$$H.COOH = H_2O + CO.$$

2. Formic acid reduces ammoniacal silver solutions forming a mirror of metallic silver, and mercuric chloride solution giving a white precipitate of mercurous chloride.

3. Neutral solutions of formates give a red-brown colour with ferric chloride, and on boiling, a brown precipitate of basic ferric formate (compare acetic acid).

Tartaric Acid.

CH.OH.COOH.
|
CH.OH.COOH.

134. The acid crystallises in large monoclinic prisms, readily soluble in water or alcohol. The solution turns the plane of polarised light to the right, or is dextro-rotatory. Heated rapidly, the acid melts at 167-170°, and then chars, as do the salts, and evolves vapours smelling of burnt sugar. Charring also occurs on heating with strong sulphuric acid.

REACTIONS. 1. To a neutral solution of a tartrate add calcium chloride solution, cool and shake well. Crystalline calcium tartrate separates, soluble in acetic acid, insoluble in ammonia.

2. To a neutral solution of a tartrate add silver nitrate: a white crystalline precipitate of silver tartrate is formed. This is soluble in ammonium hydrate, and the solution on warming gives a mirror of metallic silver.

3. To a solution of tartaric acid add some saturated solution of potassium chloride, cool and shake: a white crystalline precipitate of potassium hydrogen tartrate, $KC_4H_5O_6$, is obtained.

Potassium Hydrogen Tartrate.

(Cream of Tartar), $K.H.C_4H_4O_6$.

135. This salt is deposited, in the form of argol, during the fermentation of grape juice. It is nearly insoluble in alcohol, and while readily soluble in hot water, requires sixty parts of cold water. The commercial cream of tartar is made by purifying crude argol.

Dissolve 20 grs. of tartaric acid in 100 c.cs. of warm water, and filter if necessary. Divide into two equal parts, and carefully neutralise one half with a clear solution of about 13-14 grams caustic potash in 50 c.cs. water. This liquid now contains normal potassium tartrate $K_2C_4H_4O_6$. Heat to boiling, and add the other half of the tartaric acid solution, also heated, and set aside in a covered beaker to crystallise. Yield, about 20 grams.

Potassium Sodium Tartrate.

(Rochelle Salt), $K.Na.C_4H_4O_6.4H_2O$.

136. Mix 20 grams potassium hydrogen tartrate with 300 c.cs. water in a flask, and while warming add gradually a solution of 15 grams crystallised carbonate of soda, until the tartrate is completely dissolved and the solution exactly neutralised. If too much soda is introduced, add a little more of the bitartrate. Filter the hot neutral liquid and evaporate. Rochelle salt crystallises in colourless transparent prisms. Yield, about 20 grams.

The salt is readily soluble in water, and in taste resembles common salt. It is used in medicine as a mild laxative. Heated in a dry tube, it first loses the water of crystallisation and then chars. For reactions see Tartaric Acid.

Potassium Antimonyl Tartrate.

(Tartar Emetic), $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$.

137. In a 500 c.c. round flask place 20 grs. cream of tartar and an equal weight of antimony oxide. Add 400 c.cs. of water, and boil gently until no more of the oxide will dissolve, and the liquid no longer contains the acid salt. Add water from time to time to keep to the original volume. Filter hot. On cooling, small colourless rhombic octahedra of the double salt crystallise.

These lose their water of crystallisation on exposure to air, and crumble to powder.

Tartar emetic is soluble in 14 parts of water at 10°. The solution has an unpleasant metallic taste. With sulphuretted hydrogen in presence of hydrochloric acid the antimony is precipitated as orange-red antimony trisulphide. The substance is used as a mordant in cotton dyeing, and in medicine. In small doses of 0·1 to 0·7 of a grain its action is sudorific, but in larger doses of 1-3 grains it acts as an emetic. An excess is poisonous.

Citric Acid.

$C_6H_8O_7.H_2O$.

138. This crystallises in large rhombic prisms with one molecule of water of crystallisation. It is soluble in 4 parts of

water at 20°, and easily soluble in alcohol. The anhydrous acid melts at 153°, and at higher temperatures darkens and decomposes.

REACTIONS. 1. Heated with strong sulphuric acid, citrates evolve carbon monoxide and carbon dioxide, and are slowly blackened.

2. Calcium chloride in neutral solutions gives no precipitate in the cold, but on boiling, a white, crystalline precipitate of calcium citrate, $Ca_3(C_6H_5O_7)_2$, is produced.

3. Silver nitrate gives with neutral solutions of citrates a white, curdy precipitate of silver citrate. This is soluble in ammonia, but is reduced only after long-continued boiling.

Potassium Ferrocyanide.

(Yellow Prussiate of Potash), $K_4FeC_6N_6 . 3H_2O$.

139. This salt is the starting substance for the preparation of most of the cyanogen compounds. It was formerly prepared by igniting carbonised nitrogenous animal matter (horn and leather shavings, hoofs, blood, etc.) with crude potash and iron. Ferrocyanides are now produced in various ways from the hydrocyanic acid in crude coal gas.

It may be obtained by adding a solution of pure ferrous sulphate to one of potassium cyanide until a slight permanent precipitate is produced. Heat to boiling, filter and evaporate the clear filtrate. On cooling, potassium ferrocyanide crystallises in large yellow monoclinic prisms, with three molecules of water of crystallisation. This water is expelled on heating to 100°, and the crystals disintegrate to a white power.

$$FeSO_4 + 2KCN = Fe(CN)_2 + K_2SO_4,$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Potassium Ferricyanide.

(Red Prussiate of Potash), $K_3FeC_6N_6$.

140. By oxidation of the iron in the previous substance, the ferrocyanide passes into ferricyanide of potassium. This may be effected by passing chlorine gas into a solution of potassium ferrocyanide until the liquid is dark red in colour, and a drop

no longer gives a blue colouration with a drop of ferric chloride. The liquid now contains potassium ferricyanide and chloride.

$$2K_4FeCy_6 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl.$$

On evaporating the clear liquid the ferricyanide crystallises in red rhombic prisms.

Another method consists in oxidising the ferrocyanide by boiling with freshly prepared lead peroxide. 25 grams potassium ferrocyanide are dissolved in 400 c.cs. water, 10 grams of lead peroxide mixed to a paste with water are added, and the mixture is boiled on a sand-bath until no trace of ferrocyanide can be detected in a filtered portion of the liquid, after acidifying with dilute hydrochloric acid. The liquid is now strongly alkaline owing to the formation of caustic potash, which dissolves some of the lead monoxide.

$$2K_4FeCy_6 + PbO_2 = 2K_3FeCy_6 + K_2PbO_2.$$

Pass a stream of carbon dioxide through the liquid during the boiling until all the lead is precipitated, and filter. Crystallise the potassium ferricyanide as in the first method. Yield about 20 grs.

C. PHYSICAL MEASUREMENTS.

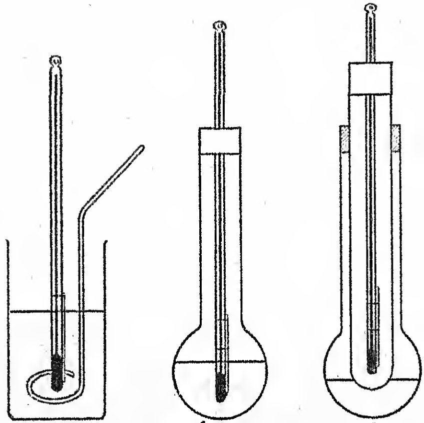
Determination of Melting Point.

141. The melting point of a substance is that constant temperature at which the solid passes into the liquid form. This temperature is most accurately determined by using a large quantity (at least 20 grs.) of the material, the vessel containing it being heated in a bath the temperature of which is a few degrees higher than that of the melting point required.

For ordinary laboratory purposes the melting point may be found with a sufficient degree of accuracy by placing some of the powdered substance in the closed end of a thin-walled capillary tube, made by drawing out a test-tube to a diameter of 1·5-2 mm. This small tube is then placed alongside of an accurate thermometer, and kept in position by a ring of rubber, cut from narrow rubber tube, and the two together are immersed in a

small beaker or tube of sulphuric acid or glycerin (Fig. 37, *a*). The ring of rubber may even be dispensed with, and the surface tension of the liquid will keep the two tubes in contact. The bath should be stirred by means of a glass stirrer, and very slowly heated over a small flame.

Instead of a beaker a long, wide-necked glass bulb (Fig. 37, *b*) may be used ; and the stirring dispensed with. To secure more uniform heating, the thermometer with capillary may be placed



a b c

Fig. 37.

in a test-tube, which in turn is placed in the acid, which should just touch the bottom of the test-tube (Graebe, Fig. 37, *c*).

The temperature at which melting begins is the true melting-point. This is constant for a pure substance, but is almost always considerably lowered by the presence of impurities.

For the purpose of identifying a substance with a known body, place three capillary tubes in contact with the thermometer, containing respectively the known substance, the unknown, and an intimate mixture of the two. If identical, all three will melt together, even on reheating. If not, the mixture will melt at a lower temperature, in general, than either of the others.

Determination of Boiling Point.

142. The boiling point of a substance is that temperature at which the vapour pressure of the substance is equal to the external pressure upon it. For a pure substance this temperature is constant at any specified pressure, and is in general raised with an increase of the pressure.

When at least 10-20 c.cs. of the liquid are available, the usual method of determining the boiling point is to distil in a small distilling flask, heated by a small flame in contact with

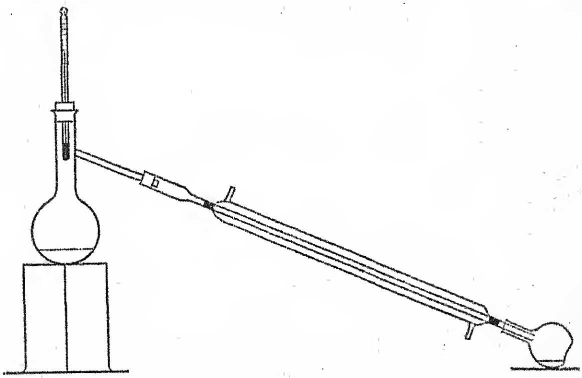


Fig. 38.

the bottom of the flask. To ensure regular boiling, some small pieces of porous clay, or clippings of platinum foil, should be placed in the liquid. The temperature is indicated by a thermometer inserted in the neck, with the bulb just below the side-tube of the flask. The bulb thus becomes coated with a film of the pure liquid in contact with its saturated vapour, and the true boiling point is found. Boiling, however, must be sufficiently rapid to keep the bulb entirely covered with vapour. Short range thermometers, the whole mercury column of which can be immersed in the vapour, are to be preferred. No correction for the emergent column of mercury is then necessary.

Correction of observed boiling point. If the mercury column emerges from the flask, which is generally the case if an

ordinary long-range thermometer is employed, this mercury is at a lower temperature than that in the bulb, and the indication of the thermometer is too low. A correction must therefore be made. This is obtained by finding the mean temperature (t) of the emergent column, by means of a small thermometer lashed to the large one (Fig. 39), so that its bulb is half way up the emergent column. Then

Fig. 39.

$$\text{Correction} = 0{\cdot}000153(T-t)N^\circ\ \text{C.},$$

where T is the observed boiling point, t the mean temperature of the cooled column, and N the number of degrees in the cooled column.

To obtain the boiling point under standard pressure the necessary correction is given by the expression

$$dt = \frac{T \, . \, dp}{9120},$$

where T is the observed boiling point on the absolute scale, and dp the difference between the observed and standard pressures.

143. When the quantity of liquid available is too small to allow of a boiling point determination by the above method, others may be used. In the method of Chapman Jones[1] a bent tube (Fig. 40) contains a small quantity of the liquid, which is conveyed to the closed end of the inverted tube, and the open end is then placed under mercury in a small dish. The whole is now introduced in this position into the bath, which is then heated to the boiling point of the liquid. The vapour of the liquid expels all the air, and on cooling, mercury enters the tube. If any air bubbles remain, the operation is repeated. The tube is then carefully removed, the liquid made to occupy the closed end, and some mercury ejected until the mercury level is lower in the open than in the closed limb. The tube is then heated slowly in the bath, in the position shown, until the mercury stands at the same level in both limbs. Since the vapour pressure of the liquid must now equal the atmospheric pressure, the temperature of the bath is the boiling point of the liquid.

[1] *Trans. Chem. Soc.* 1878, 175.

Several observations should be made, with both rising and falling temperature. The quantity of liquid used must be sufficient to leave some unvaporised, that is, the vapour must be saturated.

144. The method of Siwoloboff[1] gives the approximate boiling point with even one drop of the liquid. A narrow glass tube (Fig. 41) is sealed at one end, the liquid introduced, and a capillary tube, sealed about 1 cm. from the lower end, is placed in it. The tube is then fastened to a thermometer, so that the bulb is at the level of the liquid, and heated in a bath. Air

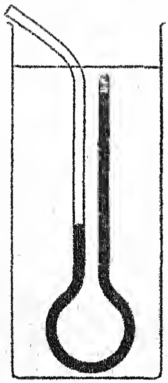


Fig. 40.

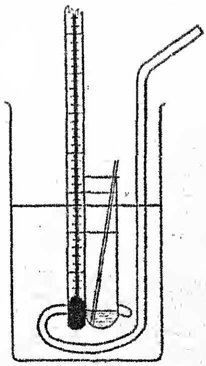


Fig. 41.

bubbles escape from the lower end of the capillary, and these become more numerous as the temperature rises. When the boiling point is reached, a rapid stream of small bubbles of vapour is emitted from the liquid. Several observations should be made, each with a fresh capillary, and the mean taken.

Determination of Specific Gravity.

145. For the determination of this constant, some form of pyknometer or specific gravity tube is employed. The ordinary

[1] *Berichte*, 19, 795 (1886).

specific gravity bottle with perforated stopper may be used, but for accurate work a more exact instrument should be employed.

Fig. 42.

A convenient form is that shown in Fig. 42. It consists of a glass tube, with narrow neck made from thermometer tubing, and a ground-in stopper. The neck has one or more marks etched round it. To use the instrument, it is filled with distilled water, suspended by a platinum wire in a beaker of finely crushed ice and water so as to give a temperature of 0° C., and left for an hour. The water level is then adjusted to one of the marks by means of a fine capillary, the tube removed, carefully dried and allowed to stand in the balance room for half an hour before weighing. Deducting the weight of the empty tube, the weight of the water is found. The dry tube is now filled with the liquid to be examined, placed in the bath for an hour and the volume adjusted as before. It is customary to determine the constant also at another temperature, 15° or 20°. The tube, after weighing with the liquid, is placed in a bath at the required temperature and some of the liquid removed.

Another form of pyknometer very commonly used is Perkin's modification (Fig. 43) of the Sprengel tube. This consists of a U-tube, the ends of the two limbs being connected to capillary tubes which are bent at 135° with them, and which are therefore at right angles to each other. On one of the capillaries is a small bulb, and a mark etched between this and the upper end of the limb. The ends of the capillaries are furnished with ground-on caps. The instrument is filled by dipping the plain capillary in the liquid, and applying suction at the

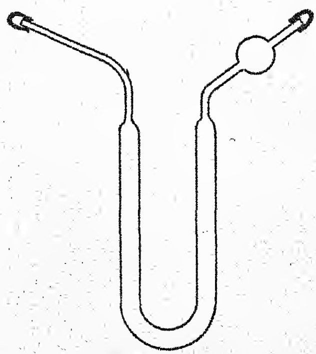


Fig. 43.

other, until the bulb is half filled. It is then placed in the ice bath, and after an hour (with caps on) the volume is adjusted by tilting the tube so that the plain capillary is horizontal, the other being vertical, and withdrawing liquid by means of filter paper placed in contact with the end of the capillary, until the liquid in the bulbed capillary has fallen exactly to the mark. Then replace the caps, dry the tube carefully and weigh after standing in the balance room for half an hour.

From the weight of water at 0° C., the weight at 4° C. should be calculated, and the density referred to this. For example, for alcohol

$$D^0/_4 = 0{\cdot}806\ ;\quad D^{20}/_4 = 0{\cdot}789.$$

Determination of Vapour Density.

146. This forms a ready method for the determination of the molecular weight of a substance, and is easily found, correct to within 5 per cent., by Victor Meyer's method.

A glass tube with cylindrical bulb *A* (Fig. 44) of at least 100 c.cs. capacity is furnished near the top with a capillary delivery tube and a short side tube through which a glass rod moves in a rubber fastener. The tube is supported in a wider tube *B*, in which a liquid is boiled, the vapour from which heats *A*. The boiling point of the liquid in *B* should be at least 20-30° above that of the substance to be examined. The bottom of *A* is covered with dry sand or asbestos, to break the fall of

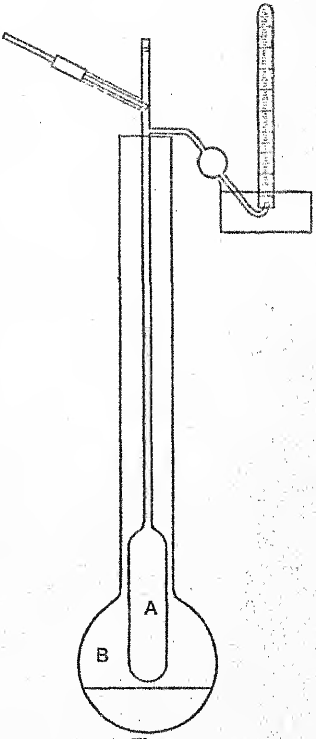


Fig. 44.

the small weighed tube, and the bath is then heated to the required temperature until no more air bubbles escape from the delivery tube. The substance is weighed in a small stoppered tube or bulb, and placed in the upper end of *A*, resting on the glass rod, and *A* then closed. When all is ready, the glass rod is withdrawn to allow the substance to drop, and at once replaced. Vaporisation should take place rapidly, and the expelled air is collected in a graduated tube placed over the end of the capillary. If this occupies too much time, diffusion of the vapour into the upper part of *A* will affect the result. When no more air is expelled, remove the measuring tube to a tall cylinder filled with water, allow it to stand in water 15 minutes, and then take the temperature of the water and the volume of the air, first adjusting the level of water in the tube to that in the cylinder. In making this adjustment, do not touch the tube with the fingers.

Calculation of the vapour density.

Let W = weight of substance used.

" V = volume of air collected.

" t = temperature of this air.

" p = barometric pressure.

" a = vapour pressure of water at $t°$.

Then the vapour density of the substance referred to hydrogen as unity is

$$D = \frac{W(273+t)760}{V(p-a)273 \times 0.0000896}.$$

The molecular weight, referred to that of hydrogen as 2, is twice the vapour density.

Determination of Molecular Weights of Organic Acids.

147. The sodium and potassium salts of the simple organic acids are destroyed by ignition, leaving the carbonate of the metal. From the weight of this, the molecular weight of the acid may be deduced, but in may cases the carbon set free during the ignition is difficult to burn away completely. It is better to use the silver salt, which leaves a residue of metallic

silver. A weighed quantity (W) of the dry salt is heated in a porcelain crucible, and the residue (R) is weighed. The loss in weight represents the radical of the acid, and the equivalent weight of the acid is therefore

$$E = \left\{ \frac{107 \cdot 93(W - R)}{R} \right\} + 1.$$

If the equivalent weight is multiplied by the basicity of the acid, the molecular weight will be found.

SECTION II.

QUALITATIVE ANALYSIS.

INSTRUCTIONS TO STUDENTS.

In the section on Qualitative Analysis those reactions of the metals and acids having no bearing on the subsequent analysis have been omitted. The principal product or products of the reactions are given, but the equations, except the more difficult, have been left to be entered by the student.

Reference should be made to the table in par. **201**, which indicates the solubilities of the principal salts of the metals, in order to obtain a clear understanding of the reactions on which the analysis depends. From the reactions given, other methods of separation should also be devised by the student.

In the analysis of a salt, before commencing the separation of the metals into groups, the student should carry out the dry reactions given, but these should not occupy more than ten minutes. From these tests he will obtain indications of the presence or absence of many of the metals, and may thus save much labour in the subsequent operations.

The detection of the acids should follow that of the metals, and as there is here no definite separation into groups, the student, after applying the preliminary tests, should write in his notes a list of those acids which have not been definitely shown to be absent, and then proceed to test for each separately.

At the end of an analysis the properties of the substance given should be written in a column, and opposite these the properties of the substances found which may account for them.

In this way the student will in many cases be able to ascertain the individual salts present, and not only the metals and acids separately.

The student should not omit to record any observation because at the time it does not convey any information to him.

REACTIONS OF THE METALS.

THE SILVER GROUP.

Metals whose chlorides are insoluble in water (Note, lead chloride is slightly soluble in cold water, much more readily in hot water).

Lead.

Pb, 207·1.

148. DRY REACTION.

Heated on charcoal, lead compounds are readily reduced to the metal, which is soft, malleable, and easily marks paper.

REACTIONS IN SOLUTION. Use a solution of lead acetate or nitrate, $(CH_3COO)_2Pb$ or $Pb(NO_3)_2$.

1. **Hydrochloric acid** gives a white precipitate of lead chloride, $PbCl_2$, soluble in hot water, crystallising in white needles on cooling.

2. **Sulphuretted hydrogen** produces a black precipitate of lead snlphide, PbS, converted by boiling with dilute nitric acid into nitrate and sulphate. In strongly acid solutions the precipitate is first reddish brown, $xPbCl_2 . yPbS$.

3. **Sulphuric acid** precipitates white lead sulphate, $PbSO_4$, slightly soluble in water, insoluble in 50 per cent. alcohol. It is soluble in a solution of ammonium acetate or tartrate, or in strong potassium hydrate or hydrochloric acid.

4. **Sodium hydrate** produces a white precipitate of lead hydrate, $Pb(OH)_2$, soluble in excess forming sodium plumbite, $Pb(ONa)_2$.

5. **Potassium iodide** gives a yellow crystalline precipitate of lead iodide, PbI_2, soluble in hot water, and recrystallising in shining yellow plates.

6. **Potassium chromate** precipitates yellow lead chromate, $PbCrO_4$, soluble in dilute nitric acid or in sodium hydrate.

7. **Sodium carbonate** forms a white precipitate of basic lead carbonate.

Silver.

Ag, 107·88.

149. DRY REACTION.

Heated on charcoal, silver compounds are readily reduced to the metal, which may be obtained as a bead at a high temperature. The bead is bright, white and hard.

REACTIONS IN SOLUTION. Use a solution of silver nitrate, $AgNO_3$.

1. **Hydrochloric acid** gives a white precipitate of silver chloride, AgCl, readily soluble in ammonium hydrate, and insoluble in nitric acid.

2. **Sulphuretted hydrogen** precipitates black silver sulphide, Ag_2S, soluble in hot nitric acid.

3. **Sodium hydrate** produces a dark grey precipitate of silver oxide, Ag_2O, readily soluble in ammonia, giving silver ammonium hydrate, NH_3AgOH.

4. **Potassium chromate** gives a brick-red precipitate of silver chromate, Ag_2CrO_4, readily soluble in dilute nitric acid, decomposed by solutions of alkali chlorides into silver chloride and a soluble chromate (see use as indicator, par. **264**).

5. **Sodium carbonate** gives a white precipitate of silver carbonate.

Mercury.

Hg, 200.

150. DRY REACTION.

Many mercury salts volatilise unchanged on heating, while others decompose, so that when heated in a dry tube they may give a white sublimate, $HgCl_2$, a yellow sublimate, HgI_2, or a sublimate of metallic mercury, HgO, $Hg(NO_3)_2$, etc. If heated with sodium carbonate, all mercury salts yield metallic mercury.

REACTIONS IN SOLUTION.

Mercurous compounds. Use a solution of mercurous nitrate, $HgNO_3$.

1. **Hydrochloric acid** precipitates white mercurous chloride, HgCl (calomel), soluble in aqua regia. It is turned black by ammonia forming mercurous ammonium chloride, NH_2Hg_2Cl.

$$2HgCl + 2NH_3 = NH_2Hg_2Cl + NH_4Cl.$$

2. **Sodium hydrate** gives a black precipitate of mercurous oxide, Hg_2O.

3. **Ammonium hydrate** produces a black precipitate of mercurous ammonium nitrate, $NH_2Hg_2NO_3$.

$$2HgNO_3 + 2NH_4OH = NH_2Hg_2NO_3 + NH_4NO_3 + 2H_2O.$$

4. **Sodium carbonate** precipitates mercurous oxide.

5. **Potassium chromate** gives a dark-red precipitate of mercurous chromate, Hg_2CrO_4, which decomposes on ignition, leaving chromium sesquioxide, Cr_2O_3.

OXIDATION OF MERCUROUS SALTS.

Mercurous salts are easily oxidised to mercuric salts, *e.g.* mercurous chloride dissolves in chlorine water or aqua regia, forming the soluble mercuric chloride, $HgCl_2$. Mercurous salts are readily reduced to mercury by stannous chloride, which is oxidised to stannic chloride.

$$2HgNO_3 + SnCl_2 + 2HCl = 2Hg + SnCl_4 + 2HNO_3.$$

SEPARATION OF THE METALS OF THE SILVER GROUP.

151. The separation and detection of the metals of this group depend upon :

(*a*) The solubility of lead chloride in hot water, silver and mercurous chlorides being insoluble ;

(*b*) The solubility of silver chloride in ammonium hydrate, mercurous chloride being insoluble.

(*c*) The formation of the black compound of mercurous chloride with ammonia.

THE COPPER GROUP.

Metals whose sulphides are insoluble in cold dilute acids.

Mercury.

Hg.

152. Mercuric Compounds. DRY REACTIONS. (See mercurous compounds.)

REACTIONS IN SOLUTION. Use a solution of mercuric nitrate $Hg(NO_3)_2$, or chloride, $HgCl_2$.

To a portion of the solution add hydrochloric acid; note the result. Repeat this procedure with the other metals of the group.

1. **Sulphuretted hydrogen** produces a black precipitate of mercuric sulphide, HgS, insoluble in nitric or hydrochloric acid, but readily soluble in aqua regia. It is converted by nitric acid to a white substance, $Hg(NO_3)_2 . HgS$. In strongly acid solutions of mercuric salts the precipitate is first white, then yellow, reddish brown, and finally black, owing to the formation of compounds of the mercuric salt and mercuric sulphide, $xHgCl_2 . yHgS$.

2. **Sodium hydrate** precipitates yellow mercuric oxide, HgO.

3. **Ammonium hydrate** gives a white precipitate of mercuric ammonium chloride, NH_2HgCl.

4. **Potassium iodide** produces a bright red precipitate of mercuric iodide, HgI_2, soluble in excess of potassium iodide or of mercuric chloride.

5. **Stannous chloride** gives a white precipitate of mercurous chloride, and by further reduction, grey metallic mercury.

6. **Sodium carbonate** precipitates mercuric oxide.

7. A piece of bright **copper** placed in an acidified solution of a mercury salt becomes coated with a grey deposit of mercury, which on rubbing acquires a bright surface.

Bismuth.

Bi, 208·0.

153. DRY REACTIONS.

1. Heated in a dry tube bismuth salts are decomposed, leaving the oxide, which is orange red while hot, pale yellow on cooling.

2. Heated on charcoal bismuth compounds are easily reduced to metal, which has a slight red tinge and is brittle. A yellow incrustation of the oxide is also formed.

REACTIONS IN SOLUTION. Use a solution of bismuth nitrate, $Bi(NO_3)_3$, or bismuth chloride, $BiCl_3$. Test as before with hydrochloric acid.

1. **Sulphuretted hydrogen** gives a dark brown precipitate of the sulphide, Bi_2S_3, soluble in nitric acid.

2. **Ammonium hydrate** precipitates white bismuth hydrate, $Bi(OH)_3$, insoluble in excess.

3. Excess of **water** causes precipitation of a white oxysalt (as $BiOCl$).

4. **Sodium carbonate** gives a white precipitate of basic carbonate.

Copper.

Cu, 63·57.

154. Dry Reactions.

1. Heated on charcoal, copper salts leave a black residue of copper oxide, CuO, which may be reduced, especially with fusion mixture and potassium cyanide in the reducing flame, to red scales of copper.

Potassium cyanide acts as a reducing agent, uniting with oxygen to form potassium cyanate.

$$KCN + O = KCNO.$$

2. Moistened with hydrochloric acid and heated on platinum wire, copper compounds colour the flame blue. If not present as the halogen compounds, the flame is green.

3. Heated in a borax bead in the oxidising flame, the bead is green while hot, blue on cooling. In the reducing flame a red bead containing small particles of copper is obtained.

Reactions in Solution. Use a solution of copper sulphate $CuSO_4 . 5H_2O$.

Test with hydrochloric acid.

1. **Sulphuretted hydrogen** produces a black precipitate of cupric sulphide, CuS, soluble in nitric acid and in potassium cyanide.

2. **Ammonium hydrate** precipitates a bluish green basic salt, $CuSO_4 . Cu(OH)_2$, which dissolves in excess, forming a deep blue solution containing the compound $CuSO_4 . 4NH_3 . H_2O$. This blue colour is destroyed by potassium cyanide.

3. **Sodium hydrate** gives a light blue precipitate of hydrate, $Cu(OH)_2$, insoluble in excess. It turns black on heating, giving hydrated copper oxide, $2CuO . H_2O$.

4. **Potassium ferrocyanide** produces a reddish brown precipitate of cupric ferrocyanide, $Cu_2Fe(CN)_6$.

5. **Sodium carbonate** precipitates a green basic carbonate.

Cadmium.

Cd, 112·4.

155. DRY REACTION.

Heated on charcoal, cadmium compounds give a brown incrustation of the oxide, CdO.

REACTIONS IN SOLUTION. Use a solution of cadmium chloride, $CdCl_2$, or sulphate, $CdSO_4$.

Test with hydrochloric acid.

1. **Sulphuretted hydrogen** gives a yellow precipitate of cadmium sulphide, CdS, soluble in dilute mineral acids, and therefore not precipitated in strongly acid solutions.

2. **Ammonium hydrate** precipitates white cadmium hydrate, $Cd(OH)_2$, soluble in excess, insoluble in sodium hydrate (distinction from zinc).

3. **Sodium carbonate** produces a white precipitate of cadmium carbonate, $CdCO_3$.

4. **Potassium cyanide** first precipitates a white cyanide, which dissolves in excess, forming the double salt

$$2KCN \,.\, Cd(CN)_2.$$

From this solution sulphuretted hydrogen precipitates the sulphide (distinction from copper).

Arsenic.

As, 75.

156. DRY REACTIONS.

1. Heated in a dry tube, arsenic compounds volatilise, giving a sublimate. If mixed with fusion mixture and potassium cyanide and heated, a sublimate of arsenic is formed.

2. Heated on charcoal, arsenic compounds partly sublime and are partly reduced, giving arsenic, which then burns to the oxide. Some of the vapour of arsenic is, however, mixed with the oxide, and may be recognised by its garlic odour.

REACTIONS IN SOLUTION.

Arsenious compounds. Use a solution of sodium arsenite, Na_3AsO_3.

Test with hydrochloric acid.

1. **Sulphuretted hydrogen** gives in acid solutions a yellow precipitate of arsenic trisulphide, As_2S_3, insoluble in strong hydrochloric acid, but soluble in ammonium sulphide, forming sodium thioarsenite.

$$As_2S_3+3(NH_4)_2S=2(NH_4)_3AsS_3.$$

With yellow ammonium sulphide, thioarsenate is produced.

$$As_2S_3+3(NH_4)_2S+S_2=2(NH_4)_3AsS_4.$$

It is also soluble in sodium hydrate, forming a mixture of arsenite and thioarsenite.

$$As_2S_3+6NaOH=Na_3AsS_3+Na_3AsO_3+3H_2O.$$

From these solutions the trisulphide or pentasulphide is precipitated by hydrochloric acid.

$$2(NH_4)_3AsS_3+6HCl=As_2S_3+6NH_4Cl+3H_2S.$$
$$2(NH_4)_3AsS_4+6HCl=As_2S_5+6NH_4Cl+3H_2S.$$
$$Na_3AsS_3+Na_3AsO_3+6HCl=As_2S_3+6NaCl+3H_2O.$$

2. **Silver nitrate** produces from neutral solutions a yellow precipitate of silver arsenite, Ag_3AsO_3, soluble in ammonium hydrate or nitric acid.

3. **Copper sulphate** precipitates Scheele's green, $CuHAsO_3$, soluble in ammonium hydrate, ammonium chloride, or in dilute nitric acid.

Arsenic compounds. Use a solution of sodium arsenate, Na_2HAsO_4.

1. **Sulphuretted hydrogen** slowly precipitates arsenic pentasulphide, at the same time reducing some of the arsenate to arsenite, and from this precipitating arsenic trisulphide. The precipitation may be hastened by using a hot, strongly acid solution, or better, by first reducing the arsenate with sulphur dioxide, boiling off excess of the dioxide before passing sulphuretted hydrogen.

The pentasulphide is soluble in ammonium sulphide, forming thioarsenate, and in sodium hydrate forming arsenate and thioarsenate.

2. **Silver nitrate** gives a reddish-brown precipitate of silver arsenate, Ag_3AsO_4, soluble in ammonium hydrate or nitric acid.

3. **Copper sulphate** produces a pale greenish-blue precipitate of cupric hydrogen arsenate, $CuHAsO_4$, soluble in ammonium hydrate or nitric acid.

4. **Magnesia mixture** (magnesium sulphate in presence of ammonium chloride and ammonium hydrate) gives a white crystalline precipitate of magnesium ammonium arsenate, $MgNH_4AsO_4 6H_2O$, soluble in acids. When heated in oxygen, this leaves a residue of magnesium pyroarsenate, $Mg_2As_2O_7$.

5. **Ammonium molybdate** produces, when heated, a yellow precipitate of magnesium arsenomolybdate, $(NH_4)_3AsO_4 . 11MoO_3 . 6H_2O$.

Antimony.

Sb, 120·2.

157. DRY REACTIONS.

Heated on charcoal, antimony compounds give a white incrustation. The metal may be obtained, but rapidly burns.

REACTIONS IN SOLUTION.

Antimonious compounds. Use a solution of antimony trichloride, or of tartar emetic.

Test with hydrochloric acid.

1. **Sulphuretted hydrogen** produces, in acid solutions, an orange precipitate of the sulphide, Sb_2S_3, soluble in ammonium sulphide, and in sodium hydrate forming thio- and oxy-salts, the sulphide being reprecipitated by hydrochloric acid. The reactions are similar to those of arsenic. Antimony trisulphide is soluble in warm concentrated hydrochloric acid.

2. Excess of **water** causes precipitation of the white oxychloride, SbOCl, soluble in solutions of tartaric acid or tartrates (distinction from BiOCl).

3. **Silver nitrate** gives, with alkaline solutions, a black precipitate of silver oxide and silver.

4. **Sodium hydrate** or carbonate forms a white precipitate of antimonious oxide, Sb_4O_6, soluble in excess of the former, producing sodium metantimonite.

$$4SbCl_3 + 12NaOH = Sb_4O_6 + 12NaCl + 6H_2O.$$
$$Sb_4O_6 + 4NaOH = 4NaSbO_2 + 2H_2O.$$

5. If, in a solution of an antimony salt, a piece of zinc be placed in contact with a piece of platinum foil, the antimony will be deposited on the platinum as a brown stain.

Antimonic compounds. Use a solution of potassium metantimonate, $KSbO_3$.

1. **Sulphuretted hydrogen** produces, in an acidified solution, an orange-red precipitate, consisting of the pentasulphide, the trisulphide and sulphur. The pentasulphide dissolves in ammonium sulphide, forming thioantimonate, $(NH_4)_3SbS_4$. It is also soluble in sodium hydrate, forming a mixture of sodium antimonate, thioantimonate, and hydrosulphide.

2. **Silver nitrate** gives a white precipitate of silver antimonate, Ag_3SbO_4.

3. **Sodium carbonate** produces a white precipitate of metantimonic acid, $HSbO_3$.

Tin.

Sn, 119.

158. DRY REACTION.

Heated on charcoal, the metal is obtained with difficulty, a white incrustation being generally formed.

REACTIONS IN SOLUTION.

Stannous salts. Use a solution of stannous chloride, $SnCl_2$.

Test with hydrochloric acid.

1. **Sulphuretted hydrogen** precipitates dark-brown stannous sulphide, SnS, soluble in *yellow* ammonium sulphide, forming thiostannate, and in sodium hydrate forming stannite and thiostannite.

$$SnS + (NH_4)_2S + S = (NH_4)_2SnS_3.$$

$$2SnS + 4NaOH = Na_2SnS_2 + Na_2SnO_2 + 2H_2O.$$

Stannous sulphide is precipitated from the latter solution by hydrochloric acid, while the former yields yellow stannic sulphide, SnS_2.

$$Na_2SnS_2 + Na_2SnO_2 + 4HCl = 2SnS + 4NaCl + 2H_2O.$$

$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$

Stannous sulphide is also soluble in hot strong hydrochloric acid, in oxalic acid, and in tartaric acid.

2. **Mercuric chloride** is reduced by stannous salts, giving mercurous chloride, and finally mercury.

3. **Sodium hydrate** gives a white precipitate of stannous hydroxide, $Sn(OH)_2$, which dissolves in excess, forming sodium stannite.

Stannic salts. Use a solution of stannic chloride, $SnCl_4$.

1. **Sulphuretted hydrogen** gives a yellow precipitate of stannic sulphide, SnS_2, soluble in ammonium sulphide, producing thiostannate, and in sodium hydrate giving stannate and thiostannate. From these solutions hydrochloric acid precipitates the stannic sulphide. The sulphide is also soluble in hot, strong hydrochloric acid.

2. **Sodium hydrate** precipitates white stannic acid, H_2SnO_3, which is converted by excess of soda into soluble sodium stannate, Na_2SnO_3.

3. In test **157, 5** for antimony, any tin which is present will be displaced from the solution by the zinc. It may then be detected by dissolving in hydrochloric acid and adding mercuric chloride. This gives a means of separating antimony from tin.

SEPARATION OF THE METALS OF THE COPPER GROUP.

159. In the detection of the metals in this group a division is first effected by the sclution of the sulphides of arsenic, antimony and tin in yellow ammonium sulphide or sodium hydrate. These three metals form a sub-group.

The detection of metals in the sub-group depends upon

(*a*) the reprecipitation of the sulphides from solution by hydrochloric acid,

(*b*) the solution of tin and antimony sulphides in strong hydrochloric acid, arsenic sulphide being insoluble,

(*c*) the solubility of tin sulphide in oxalic acid, antimony sulphide being insoluble.

The detection of the metals in the main group depends upon

(*a*) the solubility of the sulphides of lead, bismuth, copper and cadmium in nitric acid, mercuric sulphide being insoluble,

(*b*) the insolubility of bismuth hydrate in ammonium hydrate, copper and cadmium hydrates being soluble,

(*c*) the solubility of copper sulphide in potassium cyanide, cadmium sulphide being insoluble.

THE IRON GROUP.

Metals whose hydrates are insoluble in solutions of ammonium salts.

Iron.

Fe, 55·85.

160. Dry Reactions.

1. Heated on charcoal, iron compounds leave a black magnetic residue.

2. Heated in a borax bead in the oxidising flame, iron compounds give a red bead while hot, yellow on cooling. In the reducing flame the bead is bottle green.

Reactions in Solution. **Ferrous Salts.** Use a solution of ferrous sulphate, $FeSO_4 . 7H_2O$.

1. To a portion of the solution add dilute hydrochloric acid and pass sulphuretted hydrogen. Boil off the sulphuretted hydrogen or, take a fresh portion of the solution and add ammonium chloride NH_4Cl and NH_4OH **ammonium hydrate.** When the latter is added incomplete precipitation of ferrous hydrate occurs. This precipitate is at first dirty white, changing to pale green, grey, and finally brown, owing to oxidation to ferric hydrate, $Fe(OH)_3$. $Fe + NH_4OH + NH_4Cl = Fe(OH)_3$

2. **Sodium hydrate** gives a similar precipitate.

3. **Ammonium sulphide** precipitates black ferrous sulphide, FeS, soluble in dilute acids.

4. **Sodium carbonate** gives a white precipitate of ferrous carbonate, $FeCO_3$, which rapidly oxidises.

5. **Potassium ferrocyanide** forms a white precipitate of potassium ferrous ferrocyanide, $K_2Fe[Fe(CN)_6]$, which rapidly turns blue through oxidation. Owing to this rapid oxidation the precipitate produced in the ordinary way is never white.

$$K_4Fe(CN)_6 + FeSO_4 = K_2Fe[Fe(CN)_6] + K_2SO_4.$$

6. **Potassium ferricyanide** forms a deep blue precipitate of ferrous ferricyanide (Turnbull's blue).

$$2K_3Fe(CN)_6 + 3FeSO_4 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4.$$

See the use of potassium ferricyanide as indicator in volumetric work (par. 260).

Ferric salts. Use a solution of ferric chloride, $FeCl_3$.

1. To a portion of the solution add hydrochloric acid and then pass sulphuretted hydrogen. Note the change in colour and the precipitate of sulphur. The ferric salt has been reduced to a ferrous salt,

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

Boil off the sulphuretted hydrogen, add two or three drops of concentrated nitric acid, heat and add ammonium chloride and **ammonium hydrate.** A brown precipitate of ferric hydrate is obtained, the nitric acid having reoxidised the ferrous to ferric salt.

$$6FeCl_2 + 6HCl + 2HNO_3 = 6FeCl_3 + 4H_2O + 2NO.$$

In analytical work the ferrous salts must always be oxidised to ferric, as the former are not completely precipitated by ammonium hydrate.

Ferric hydrate is soluble in hydrochloric acid, insoluble in sodium hydrate. When heated alone it leaves the oxide Fe_2O_3 which is unaffected by fusion with fusion mixture and potassium nitrate.

2. **Sodium hydrate** gives a precipitate of ferric hydrate, insoluble in excess of the reagent.

3. **Sodium carbonate** produces the same precipitate with evolution of carbon dioxide.

4. **Ammonium sulphide** gives a black precipitate of ferrous sulphide, sulphur also being precipitated.

$$2FeCl_3 + 3(NH_4)_2S = 2FeS + 6NH_4Cl + S.$$

5. **Potassium ferrocyanide** precipitates deep blue ferric ferrocyanide (Prussian blue), $Fe_4[Fe(CN)_6]_3$, insoluble in hydrochloric acid but decomposed by caustic alkalies,

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 4Fe(OH)_3 + 3K_4Fe(CN)_6.$$

6. **Potassium ferricyanide** forms no precipitate, but the solution turns brown (compare ferrous and see use as indicator).

7. **Potassium thiocyanate** gives a blood-red colouration, due to the soluble ferric thiocyanate $Fe(SCN)_3$. This is a very delicate test for iron.

8. **Sodium phosphate** precipitates pale buff coloured ferric phosphate, $FePO_4$, which is soluble in mineral acids, but insoluble in acetic acid or ammonia.

Ferrous salts are easily oxidised (chlorine or nitric acid being generally used) to ferric salts, and ferric salts are easily reduced to ferrous.

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$
$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

Chromium.

Cr, 52·1.

161. DRY REACTIONS.

1. Heated on charcoal, chromium compounds leave a dark green residue.

2. Heated on platinum or porcelain with fusion mixture and a little nitre, a yellow mass of potassium and sodium chromates is obtained.

3. Heated in a borax bead, an emerald green bead is formed in either flame ($Cr_2O_3 . B_2O_3$).

REACTIONS IN SOLUTION. Use a solution of chrome alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$.

1. As with iron, add hydrochloric acid, then sulphuretted hydrogen (no change), boil off the latter and add ammonium chloride and **ammonium hydrate**. A bluish-green precipitate of chromic hydrate, $Cr(OH)_3$, is formed, slightly soluble in excess, giving a lilac-coloured liquid, from which the chromium hydrate is completely precipitated by boiling. Chromium hydrate is soluble in dilute acids.

2. **Sodium hydrate** gives the same precipitate, which readily dissolves in excess to a bright green solution of sodium chromite $Cr(ONa)_3$. The hydrate begins at once to separate from this solution when boiled, but for complete precipitation long boiling is required.

3. **Ammonium sulphide** produces the same precipitate.

$$Cr_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 2Cr(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S.$$

4. **Sodium carbonate** gives a precipitate of hydrate and carbonate, which gives pure hydrate on boiling.

5. **Sodium phosphate** precipitates pale green chromium phosphate, $CrPO_4$, soluble in mineral acids, insoluble in acetic acid or ammonia.

Oxidation of Chromium Compounds.

Chromium compounds are easily oxidised to chromates, as in the dry reaction (2) or as follows:

1. Add **sodium peroxide** to a cold solution of a chromic salt, and boil till effervescence ceases. Sodium chromate is formed.

$$2Cr(OH)_3 + 3Na_2O_2 = 2Na_2CrO_4 + 2NaOH + 2H_2O.$$

A method of separation of Fe, Al, and Cr consists in separating *the Cr and Al from the iron as sodium chromate* and sodium aluminate by the action of sodium peroxide.

2. **Sodium hypochlorite,** or sodium hydrate and chlorine water or bromine water oxidise chromic salts.

$$2Cr(OH)_3 + 3NaOCl + 4NaOH = 2Na_2CrO_4 + 3NaCl + 5H_2O.$$

Chromates.

Reactions in Solution.

1. **Sulphuretted hydrogen** in presence of an acid reduces the chromate to a chromic salt, the colour changing to green, and sulphur being precipitated.

$$2K_2CrO_4 + 10HCl + 3H_2S = 4KCl + 2CrCl_3 + 8H_2O + 3S.$$

2. **Sulphurous acid** also reduces chromates to green chromic salts, but no sulphur is precipitated.

$$2K_2CrO_4 + 3H_2SO_3 + 2H_2SO_4 = 2K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O.$$

3. **Silver nitrate** in neutral solutions forms a red precipitate of silver chromate, soluble in nitric acid.

4. **Lead nitrate** gives a yellow precipitate of lead chromate.

5. **Barium chloride** precipitates yellow barium chromate, soluble in hydrochloric acid.

6. **Mercurous nitrate** produces a dark-red precipitate of mercurous chromate.

Chromates are easily reduced to chromic salts, and therefore chromates and chromic acid are powerful oxidising agents (see volumetric work).

DISTINCTION BETWEEN CHROMATES AND DICHROMATES.

Chromates are converted into dichromates on addition of acid, the colour changing from yellow to orange. Dichromates are changed to chromates by alkalies.

Chromates are neutral to litmus, while dichromates are acid. Solutions of dichromate decompose carbonates, carbon dioxide being evolved.

DETECTION OF A CHROMIUM SALT AND CHROMATE TOGETHER.

Boil a little of the substance with sodium carbonate solution and filter. If chromates be present the filtrate is yellow; confirm with a lead salt. The precipitate will contain the chromium of the chromic salt as hydrate.

Aluminium.

Al, 27·1.

162. DRY REACTION.

1. Heated on charcoal, aluminium compounds leave white aluminium oxide, Al_2O_3, which when moistened with cobalt nitrate and reheated gives a blue mass of cobalt aluminate. (Silica and silicates, phosphates and borates, give a blue mass, but require to be fused.)

REACTIONS IN SOLUTION. Use a solution of alum, $K_2SO_4Al_2(SO_4)_3 24H_2O$.

1. Add hydrochloric acid, etc., as before, then ammonium chloride and **ammonium hydrate**. A white precipitate of aluminium hydrate, $Al(OH)_3$, is produced, soluble in a large excess of the reagent, but completely reprecipitated on boiling. The precipitate is also soluble in dilute acids.

2. **Sodium hydrate** gives the same precipitate, readily soluble in excess, forming sodium aluminate, Na_3AlO_3, which is decomposed by ammonium chloride, the precipitation being complete on boiling. Sodium aluminate is also decomposed by dilute acids.

3. **Ammonium sulphide** forms the same precipitate, with evolution of sulphuretted hydrogen.

4. **Sodium carbonate** produces a precipitate of hydrate and carbonate, which gives pure hydrate on boiling.

5. **Sodium phosphate** precipitates white aluminium phosphate, $AlPO_4$, soluble in mineral acids, but insoluble in acetic acid or ammonia.

SEPARATION OF THE METALS OF THE IRON GROUP.

163. The detection and separation of the metals of the iron group depend upon

(*a*) The solubility of the hydrates in hydrochloric acid.

(*b*) The precipitation from this solution of ferric and chromic hydrates by boiling with excess of sodium hydrate, aluminium remaining in solution.

(*c*) The conversion of chromic hydrate to a soluble chromate, the iron oxide being insoluble.

THE ZINC GROUP.

Metals whose sulphides are precipitated in alkaline, but not in acid solutions.

Zinc.

Zn, 65·37.

164. DRY REACTIONS.

1. Heated in a bulb tube, most zinc compounds leave a residue of oxide, which is yellow when hot and white when cold.

2. Heated on charcoal with a little sodium carbonate, zinc compounds are reduced to the metal, which is volatile and easily oxidised. No bead is formed, but an incrustation of oxide appears on the charcoal. When moistened with solution of cobalt nitrate and again heated, the residue becomes green (Rinmann's green).

REACTIONS IN SOLUTION. Use a solution of zinc sulphate, $ZnSO_4 . 7H_2O$.

To a portion of this solution add dilute hydrochloric acid, then sulphuretted hydrogen; next boil off the latter or take a fresh portion of the solution and add ammonium chloride and

ammonia. Note the results and consider their utility. Repeat this procedure with the other metals of the group.

1. **Ammonium sulphide**, or H_2S in the alkaline solution, gives a white precipitate of zinc sulphide, ZnS, insoluble in alkalies or in acetic acid, soluble in mineral acids.

2. **Sodium** or **potassium hydrate** precipitates white zinc hydroxide, $Zn(OH)_2$, soluble in excess, forming an alkaline zincate, $Zn(ONa)_2$. Sulphuretted hydrogen precipitates the zinc from this completely as sulphide.

3. **Sodium** or **potassium carbonate** produces a white precipitate of basic zinc carbonate, $2ZnCO_3 . 3Zn(OH)_2$. Some carbon dioxide gas is liberated. This precipitate is also obtained with ammonium carbonate, but is soluble in excess and in other ammonium salts.

4. **Potassium cyanide** gives a white precipitate of zinc cyanide, soluble in excess, forming the double cyanide, $ZnCy_2 . 2KCy$.

Manganese.

Mn, 54·93.

165. DRY REACTIONS.

1. All manganese compounds, heated with three parts of fusion mixture and a little nitre, on platinum or porcelain, produce a dark blue-green mass of alkaline manganate, Na_2MnO_4. If this is dissolved in water and the solution acidified with sulphuric acid, the colour changes to pink, owing to the formation of permanganate, $NaMnO_4$. (See par. 91.)

2. The borax or microcosmic bead is coloured violet to amethyst in the oxidising flame ($Mn_2O_3 . B_2O_3$), but is colourless in the reducing flame ($MnO . B_2O_3$).

REACTIONS IN SOLUTION. Use a solution of manganous chloride or sulphate. Test with hydrochloric acid, etc., as directed under zinc.

1. **Ammonium sulphide** gives a flesh-coloured precipitate of manganous sulphide, MnS, insoluble in alkalies, soluble in acetic acid or mineral acids.

2. **Sodium hydrate** precipitates white manganous hydrate, $Mn(OH)_2$, insoluble in excess, soluble in ammonium chloride.

The precipitate rapidly turns brown through oxidation to manganic hydrate, $Mn_2O_3 . H_2O$.

3. **Ammonium hydrate** gives the same precipitate in absence of ammonium salts. In presence of ammonium chloride no precipitate is obtained, but by passing air through the warm solution the manganese may be completely precipitated as sesquioxide, $Mn_2O_3 . H_2O$. For this reason it is difficult to separate iron and manganese by means of ammonium chloride and hydrate.

4. **Sodium peroxide,** sodium hypochlorite, or bromine water, added to the alkaline solution of manganous salts, oxidise the manganese to higher oxides, Mn_2O_3 or MnO_2, which are precipitated.

5. **Alkali carbonates** precipitate white manganous carbonate, $MnCO_3$, insoluble in excess, soluble in ammonium chloride.

6. **Permanganic acid reaction.** Place some lead peroxide, or red lead, in a test-tube, add dilute nitric acid and a solution of manganous salt (except haloid salts) and warm gently. Allow the lead peroxide to settle. The liquid has now a rose-pink colour, due to permanganic acid.

Permanganates.

1. **Heated alone,** these decompose into oxides of the metals and free oxygen, with some manganate.

2. **Heated gently** with **sulphuric acid,** some manganese heptoxide is first produced, the metals form sulphates, and free oxygen is evolved.

3. With strong **hydrochloric acid,** chlorides are produced, and free chlorine equivalent to the available oxygen.

$$2KMnO_4 = K_2O + 2MnO_2 + 3 . O.$$
$$2KMnO_4 + H_2SO_4 = K_2SO_4 + Mn_2O_7 + H_2O.$$
$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5 . O.$$
$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5 . Cl_2.$$

4. **All permanganates** dissolve in water, giving purple-red solutions. They are powerful oxidising agents, stable in the cold and in absence of easily oxidisable substances, but immediately reduced (decolourised) by sulphurous acid, sulphuretted hydrogen, ferrous salts, oxalic acid, etc.

5. **Hydrogen peroxide** and permanganates acidified with sulphuric acid immediately destroy each other when mixed, evolving oxygen in equivalent amounts. This reaction is employed for the estimation of hydrogen peroxide and of permanganates.

Nickel.

Ni, 58·68.

166. Dry Reactions.

1. Heated on charcoal with fusion mixture, metallic nickel is obtained as a grey magnetic powder.

2. The borax bead is coloured red-brown in the oxidising flame ($NiO . B_2O_3$), and in the reducing flame colourless but slightly opaque from metallic nickel.

Reactions in Solution. Use a solution of nickel sulphate, $NiSO_4 . 7H_2O$.

1. **Ammonium sulphide** gives a black precipitate of nickelous sulphide, NiS, slightly soluble in excess, insoluble in acetic acid, soluble with difficulty in hydrochloric acid, readily in nitric acid, aqua regia, or hydrochloric acid and potassium chlorate.

2. **Sodium hydrate** precipitates apple-green nickelous hydrate, $Ni(OH)_2$, insoluble in excess, soluble in ammonia or its salts. On ignition it leaves grey nickelous oxide, NiO.

3. **Ammonium hydrate** gives the same precipitate, soluble in excess forming a deep blue solution.

4. **Sodium carbonate** precipitates an apple-green basic carbonate of varying composition. The same is obtained with ammonium carbonate, but is soluble in excess.

5. **Potassium cyanide** produces a green precipitate of nickelous cyanide, $Ni(CN)_2$, soluble in excess of potassium cyanide, forming the complex cyanide K_2NiCy_4. Sulphuretted hydrogen gives no precipitate from this solution, the nickel forming part of the complex anion $= NiCy_4$, but the compound is completely decomposed by boiling with hydrochloric acid.

6. To the above solution in potassium cyanide add **sodium hypochlorite**, or sodium hydrate and bromine water, and warm gently. Black nickelic hydrate is precipitated.

$$2NiCy_2 + NaOCl + 5H_2O = Ni_2(OH)_6 + NaCl + 4HCy.$$

This reaction is employed to separate nickel from cobalt.

Cobalt.

Co, 58·97.

167. Dry Reactions.

1. Heated on charcoal, cobalt compounds are reduced less easily than those of nickel, giving a grey, feebly magnetic powder.

2. The borax bead is coloured deep blue in both oxidising and reducing flames ($CoO . B_2O_3$).

Reactions in Solution. Use cobaltous chloride or nitrate.

1. **Ammonium sulphide** precipitates black cobaltous sulphide, CoS, insoluble in excess or in dilute acids, soluble in aqua regia.

2. **Sodium hydrate** precipitates a blue basic salt, which absorbs oxygen from air, the colour changing to olive-green.

3. **Ammonium hydrate** gives a slight precipitate of a similar basic salt, soluble in excess, forming a red-brown solution. This absorbs oxygen on standing, and becomes red in colour.

4. **Potassium cyanide** gives a light brown precipitate of cobaltous cyanide, $CoCy_2$, soluble in excess, with formation of the double cyanide $4KCy . CoCy_2$. Dilute acids reprecipitate cobaltous cyanide.

This substance is very readily oxidised to potassium cobalticyanide, the change taking place even on boiling with water alone, but more readily in presence of a little free hydrocyanic acid; hydrogen is evolved in the absence of air:

$$2CoCy_2 + 2HCy = Co_2Cy_6 + H_2.$$

This cobaltic cyanide remains in solution as the complex potassium cobalticyanide, from which oxidising agents (NaOCl) give no precipitate.

SEPARATION OF THE METALS OF THE ZINC GROUP.

168. The detection and separation of the metals in this group depend on:

(*a*) The solubility of zinc and manganous sulphides in dilute hydrochloric acid, those of nickel and cobalt being insoluble.

(*b*) The precipitation of zinc and manganous hydroxides by sodium hydrate, the zinc compound alone being soluble in excess.

(*c*) The precipitation of nickel and cobalt as cyanides, soluble in excess of potassium cyanide, the cobalt compound being converted, by boiling, into cobaltic potassium cyanide, from which cobalt is not precipitated by heating with sodium hypochlorite, while the nickelous cyanide is oxidised to the black nickelic hydrate.

THE BARIUM GROUP.

Metals whose carbonates are insoluble in ammonium hydroxide or carbonate.

Barium.

Ba, 137·37.

169. DRY REACTION. Barium compounds give a persistent green colour to the Bunsen flame, especially when moistened with hydrochloric acid.

REACTIONS IN SOLUTION. Use a solution of barium chloride.

Test small portions of the solutions of barium, strontium and calcium with the group reagents for the foregoing groups, namely (i) hydrochloric acid, (ii) hydrochloric acid and sulphuretted hydrogen, (iii) ammonium chloride and ammonia, and (iv) ammonium sulphide. Note the results obtained.

1. **Ammonium carbonate** gives a heavy white precipitate of barium carbonate, $BaCO_3$, decomposed by acetic acid, and slightly soluble in ammonium chloride.

2. **Sulphuric acid** or a soluble sulphate ($CaSO_4$) precipitates heavy white barium sulphate, $BaSO_4$, insoluble in acids.

3. **Potassium chromate** produces a lemon-yellow precipitate of barium chromate, $BaCrO_4$, soluble in mineral acids.

4. **Ammonium oxalate** precipitates white barium oxalate, BaC_2O_4, soluble in mineral acids, or in oxalic or acetic acids when freshly precipitated.

Strontium.

Sr, 87·62.

170. Dry Reaction. Strontium compounds impart an intense crimson colour to the Bunsen flame.

Reactions in Solution. Use a solution of strontium chloride.

1. **Ammonium carbonate** gives a white precipitate of strontium carbonate, $SrCO_3$, decomposed by acetic acid.

2. **Sulphuric acid** produces a white precipitate of strontium sulphate, $SrSO_4$. The precipitation is slow from dilute solutions, and is accelerated by adding ammonium sulphate.

3. **Potassium chromate** precipitates yellow strontium chromate, $SrCrO_4$, from solutions which are not too dilute. The chromate is soluble in acetic or mineral acids.

4. **Ammonium oxalate** gives a white precipitate of strontium oxalate, SrC_2O_4, less soluble than barium oxalate, decomposed by mineral acids.

Calcium.

Ca, 40·09.

171. Dry Reaction. The Bunsen flame is coloured yellowish red by most calcium compounds, especially when moistened with strong hydrochloric acid.

Reactions in Solution. Use a solution of calcium chloride.

1. **Ammonium carbonate** precipitates white, amorphous calcium carbonate, $CaCO_3$, which becomes crystalline on standing. This is soluble in acetic acid and slightly soluble in ammonium chloride, especially on boiling.

2. **Sulphuric acid** gives from strong solutions of calcium salts a white precipitate of calcium sulphate, $CaSO_4$, soluble in much water or in ammonium sulphate solution.

3. **Potassium Chromate** causes no precipitation, calcium chromate being soluble in water.

4. **Ammonium oxalate** produces even from very dilute solutions a white crystalline precipitate of calcium oxalate, CaC_2O_4, soluble in mineral acids, insoluble in acetic acid or ammonia.

SEPARATION OF THE METALS OF THE BARIUM GROUP.

172. The separation and detection of these metals is based on:

(*a*) The insolubility of barium chromate in acetic acid, strontium and calcium chromates being soluble.

(*b*) The insolubility of strontium sulphate in water or ammonium sulphate solution, calcium sulphate being soluble.

(*c*) The insolubility of calcium oxalate in acetic acid.

THE SODIUM GROUP.

This group comprises the metals potassium, sodium, lithium and magnesium, and the complex cation ammonium, NH_4, which are not precipitated by any previous group reagent. The student should prove the latter statement for himself.

Potassium.

K, 39·1.

173. Dry Reaction. Potassium compounds colour the Bunsen flame violet. This cannot be detected in presence of sodium, unless a cobalt glass or permanganate or indigo prism be used, which does not transmit the yellow sodium light.

Reactions in Solution. Use potassium chloride.

1. **Platinic chloride** gives a heavy, golden-yellow crystalline precipitate of potassium platinichloride, K_2PtCl_6, slightly soluble in water, insoluble in acids or in alcohol. If no precipitate is obtained, evaporate to a small bulk and add an equal volume of alcohol.

2. **Tartaric acid** precipitates white crystalline potassium bitartrate, $KC_4H_5O_6$, from strong solutions, especially on shaking.

Sodium.

Na, 23·0.

174. Dry Reaction. An intense golden-yellow colour is imparted to the Bunsen flame, the light appearing through the

spectroscope as a bright double line, coinciding with the solar D line. The reaction is a very delicate one, and the colouration should be strong and persistent.

As most sodium compounds are soluble in water, the flame test chiefly is relied on for the detection of sodium.

Lithium.

Li, 7·0.

175. DRY REACTION. The Bunsen flame is coloured crimson by lithium compounds, the spectrum containing two lines, a bright crimson and a feebler orange line.

REACTIONS IN SOLUTION. Use a solution of lithium chloride. Platinum chloride or tartaric acid gives no precipitate.

1. **Sodium phosphate** gives, on boiling, a white precipitate of lithium phosphate, $2Li_3PO_4 . H_2O$, especially in presence of sodium hydrate. The precipitate is soluble in hydrochloric acid or in ammonium salts.

2. **Alkaline carbonates** precipitate from strong solutions white crystalline lithium carbonate, Li_2CO_3, insoluble in alcohol, decomposed by acids.

Ammonium.

NH_4, 18·04.

176. DRY REACTION. When heated in a dry tube, ammonium salts volatilise either wholly (those with volatile acids) or partly (those with fixed acids, as phosphoric). In the former case a sublimate will form on the cold part of the tube. On adding a little soda lime and again heating, free ammonia is obtained.

REACTIONS IN SOLUTION. Use a solution of ammonium chloride.

1. **Platinic chloride** gives a heavy, yellow crystalline precipitate of ammonium platinichloride $(NH_4)_2PtCl_6$, soluble in much water, insoluble in alcohol. On ignition, this compound leaves only spongy platinum, and is thus distinguished from the similar potassium compound, which leaves a residue of potassium chloride and platinum.

2. All ammonium salts are decomposed when ground with **sodium hydrate** or **soda lime**, evolving free ammonia.

3. **Nessler's reagent** gives a brown precipitate of dimercurammonium iodide, or a yellow or brown colouration in solutions containing mere traces of ammonia,

$$2(2KI \,.\, HgI_2) + NH_4OH + 3KOH = NHg_2I \,.\, H_2O + 7KI + 3H_2O.$$

Magnesium.

Mg, 24·32.

177. Dry Reaction. Magnesium compounds leave a white residue on charcoal, which becomes incandescent. If this is moistened with cobalt nitrate and again heated, it becomes pink. This reaction, however, is only reliable in absence of other oxides.

Reactions in Solution. Use a solution of magnesium sulphate.

1. **Ammonium hydrate** produces a partial precipitate of magnesium hydrate, $Mg(OH)_2$, soluble in ammonium chloride. Ammonium salts completely prevent this precipitation.

2. **Potassium**, sodium, calcium or barium **hydrates** precipitate magnesium hydrate almost completely. It is almost insoluble in cold or hot water, readily soluble in dilute acids.

3. **Sodium phosphate** gives a white precipitate of magnesium hydrogen phosphate, $MgHPO_4$. In presence of ammonia, magnesium ammonium phosphate, $MgNH_4PO_4 \,.\, 6H_2O$, is obtained as a white crystalline precipitate, practically insoluble in dilute ammonium hydrate, soluble in mineral acids or in acetic acid. From very dilute solutions the precipitate forms very slowly.

$$MgSO_4 + Na_2HPO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

When ignited the precipitate is decomposed into magnesium pyrophosphate, with loss of ammonia and water.

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

Detection of the Metals of the Sodium Group.

178. In this group the flame colouration is a reliable test for sodium, potassium and lithium, especially if examined by means of a spectroscope. Potassium is confirmed by the reaction with platinic chloride.

Ammonium compounds are detected in the original substance.

The only separation necessary is that of magnesium from lithium. This is effected by precipitating the magnesium in cold solution with sodium phosphate and ammonia, and the lithium by boiling the filtrate with sodium hydrate.

REACTIONS OF THE ACIDS.

Hydrochloric Acid.

HCl.

179. REACTIONS. Use sodium chloride.

1. Warmed with strong **sulphuric acid**, hydrochloric acid is liberated, and is recognised by its smell and by the fumes in moist air.

2. Warmed with strong **sulphuric acid** and **manganese dioxide**, chlorine is liberated, recognised by its smell, and its bleaching action on litmus paper.

3. **Silver nitrate** gives a white precipitate of silver chloride, $AgCl$, readily soluble in ammonium hydrate, but insoluble in nitric acid.

4. Warmed with strong **sulphuric acid** and **potassium dichromate** or chromate, a red vapour of chromyl chloride, CrO_2Cl_2, is given off (see preparation of chromyl chloride).

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \\ = 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O.$$

The vapour, when poured into a test tube containing water, gives a yellow solution of chromic acid and hydrochloric acid. If sodium hydrate be used instead of water a yellow solution of chromate and chloride will be produced.

$$CrO_2Cl_2 + 4NaOH = Na_2CrO_4 + 2NaCl + 2H_2O.$$

The chromate may be tested for by acidifying with acetic acid and adding lead acetate. (Compare the action of bromine on sodium hydrate.) This gives a means of detecting chlorides in presence of bromides.

Hydrobromic Acid.

HBr.

180. REACTIONS. Use potassium bromide.

1. Warmed with strong **sulphuric acid**, hydrobromic acid and bromine are liberated, the latter owing to oxidation of part of the hydrobromic acid by the sulphuric acid.

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2.$$

2. With sulphuric acid and **manganese dioxide**, bromine is liberated.

3. **Silver nitrate** gives a pale yellow precipitate of silver bromide, $AgBr$, soluble with difficulty in ammonium hydrate, and insoluble in nitric acid.

4. **Chlorine water** (but not sodium hypochlorite or nitrous acid) added to a solution of a bromide liberates bromine, and on shaking with carbon disulphide or chloroform a brown layer is formed. Excess of chlorine water *gradually* oxidises the bromine to bromic acid, $HBrO_3$.

Hydriodic Acid.

HI.

181. REACTIONS. Use potassium iodide.

1. Warmed with concentrated **sulphuric acid**, a little hydriodic acid is produced, and much iodine. The smell of sulphuretted hydrogen may be detected.

$$2KI + H_2SO_4 = K_2SO_4 + 2HI.$$
$$8HI + H_2SO_4 = 4H_2O + H_2S + 4I_2.$$

2. Warmed with concentrated sulphuric acid and **manganese dioxide**, iodine is liberated.

3. **Silver nitrate** gives a pale yellow precipitate of silver iodide, AgI, insoluble in ammonium hydrate or in nitric acid.

4. **Chlorine water**, sodium hypochlorite or nitrous acid liberates iodine from iodides, and on shaking with carbon disulphide, a violet layer is obtained. The chlorine water must be added drop by drop, as the iodine liberated is very readily converted into iodic acid.

$$I + 3H_2O + 5Cl = HIO_3 + 5HCl.$$

If bromine and iodine are liberated together in this manner

and shaken with carbon disulphide, the iodine colour masks that of the bromine, but by careful addition of chlorine water the colour of the iodine disappears and that due to the bromine is left.

5. **Starch paste** gives with free iodine a deep blue colouration.

6. **Copper sulphate** in presence of sulphurous acid gives a white precipitate of cuprous iodide, Cu_2I_2.

$$2CuSO_4 + 2KI + H_2SO_3 + H_2O = 2KHSO_4 + H_2SO_4 + Cu_2I_2.$$

By this means the iodide may be removed, one part of the filtrate tested with chlorine water and carbon disulphide for bromide, and another part evaporated and tested by the chromyl chloride test for chloride.

To test for the halogens in presence of a cyanide, first remove the cyanide by boiling with dilute nitric acid, or with excess of sodium bicarbonate. Or precipitate with excess of $AgNO_3$ and ignite the precipitate. Silver cyanide is decomposed, the chloride only fused. See also under Hydrocyanic acid.

Hydrofluoric Acid.

HF.

182. Reactions. Use sodium fluoride.

1. Warmed with strong **sulphuric acid,** hydrofluoric acid is liberated and may be made to etch glass. Use a leaden dish for this experiment. If a test-tube is used a greasy appearance is often noticed in the tube.

2. Heated with strong **sulphuric acid** and **sand,** silicon tetrafluoride is produced (see preparation of silica). On holding a moist glass rod near the mixture a deposit of silicic acid is seen on the rod.

3. **Calcium** or barium **chloride** gives a white precipitate of fluoride, CaF_2 or BaF_2.

4. **Silver nitrate** gives no precipitate.

Hypochlorous Acid.

HOCl.

183. Use sodium hypochlorite, NaOCl, or bleaching powder, CaCl(OCl). The peculiar smell of hypochlorites is due to free

hypochlorous acid, which is liberated by the action of atmospheric carbon dioxide gas.

$$NaOCl + CO_2 + H_2O = HOCl + NaHCO_3.$$

REACTIONS IN SOLUTION.

1. When **heated** in solution, or in the dry state, hypochlorites are converted into chlorides and chlorates:

$$6Ca(OCl)_2 = 5CaCl_2 + Ca(ClO_3)_2.$$

2. When the solution is heated with a little **cobalt oxide** (obtained by addition of cobalt nitrate solution), oxygen is evolved, and a chloride left:

$$2Ca(OCl)_2 = 2CaCl_2 + O_2.$$

3. On adding dilute **hydrochloric acid,** chlorine is liberated, which may be detected by adding to a solution of potassium iodide and starch (distinction from chlorates).

4. The acidified solution has a powerful **bleaching action** on vegetable colours—litmus and indigo are decolourised.

Chloric Acid.

$HClO_3$.

184. Use potassium chlorate, $KClO_3$.

DRY REACTION. All chlorates give off oxygen on heating, leaving chlorides. The oxygen contains traces of chlorine.

REACTIONS IN SOLUTION.

1. Heated gently with strong **sulphuric acid,** chlorine peroxide, ClO_2, is liberated, a yellowish green, explosive gas. Use only one small crystal of chlorate:

$$3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + 2ClO_2 + H_2O.$$

2. Warmed with **hydrochloric acid,** a mixture of chlorine and chlorine peroxide is obtained:

$$8KClO_3 + 24HCl = 6ClO_2 + 9Cl_2 + 8KCl + 12H_2O.$$

Indigo solution is decolourised by this mixture.

Carbonic Acid.

H_2CO_3.

185. DRY REACTIONS. Carbonates of the heavy metals give off carbon dioxide on heating.

Bicarbonates when heated alone, or when boiled in water, give off water and carbon dioxide, leaving carbonates (distinction between carbonates and bicarbonates).

REACTIONS IN SOLUTION. Use a solution of sodium carbonate, $Na_2CO_3 . 10H_2O$.

1. Dilute **hydrochloric acid** liberates carbon dioxide, which may be recognised by pouring the gas into lime water. The latter is turned milky.

2. **Silver nitrate** forms a white precipitate of silver carbonate, soluble in dilute nitric acid or in ammonium hydrate.

3. **Barium chloride** produces a white precipitate of barium carbonate, soluble in dilute hydrochloric acid.

4. **Potassium dichromate** liberates carbon dioxide from carbonates or bicarbonates, but does not liberate sulphur dioxide from sulphites. The dichromate is converted into chromate, with change of colour. Compare **186**, 5.

Sulphurous Acid.

H_2SO_3.

186. Use sodium sulphite, $Na_2SO_3 . 7H_2O$.

DRY REACTION. Heated on charcoal, a sulphide is formed; when the residue is placed on a silver coin and moistened with water, a black stain is produced.

REACTIONS IN SOLUTION.

1. Dilute **hydrochloric acid** liberates sulphur dioxide, which is recognised by its smell, and by reduction of potassium dichromate solution on a strip of filter paper held in the mouth of the test-tube.

2. **Barium chloride** gives with strong solutions a white precipitate of barium sulphite, soluble in hydrochloric acid.

3. **Silver nitrate** produces a white precipitate of silver sulphite, soluble in nitric acid and in ammonium hydrate.

4. **Chlorine water** oxidises sulphites to sulphates, which may then be examined for.

5. **Potassium dichromate** does not liberate sulphur dioxide from sulphites, but is itself reduced to green chromic sulphate. It may be used to separate sulphur dioxide and sulphuretted hydrogen from mixtures of these gases with carbon dioxide.

Bicarbonates when heated alone, or when boiled in water, give off water and carbon dioxide, leaving carbonates (distinction between carbonates and bicarbonates).

REACTIONS IN SOLUTION. Use a solution of sodium carbonate, $Na_2CO_3 . 10H_2O$.

1. Dilute **hydrochloric acid** liberates carbon dioxide, which may be recognised by pouring the gas into lime water. The latter is turned milky.

2. **Silver nitrate** forms a white precipitate of silver carbonate, soluble in dilute nitric acid or in ammonium hydrate.

3. **Barium chloride** produces a white precipitate of barium carbonate, soluble in dilute hydrochloric acid.

4. **Potassium dichromate** liberates carbon dioxide from carbonates or bicarbonates, but does not liberate sulphur dioxide from sulphites. The dichromate is converted into chromate, with change of colour. Compare **186**, 5.

Sulphurous Acid.

H_2SO_3.

186. Use sodium sulphite, $Na_2SO_3 . 7H_2O$.

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REACTIONS IN SOLUTION.

1. Dilute **hydrochloric acid** liberates sulphur dioxide, which is recognised by its smell, and by reduction of potassium dichromate solution on a strip of filter paper held in the mouth of the test-tube.

2. **Barium chloride** gives with strong solutions a white precipitate of barium sulphite, soluble in hydrochloric acid.

3. **Silver nitrate** produces a white precipitate of silver sulphite, soluble in nitric acid and in ammonium hydrate.

4. **Chlorine water** oxidises sulphites to sulphates, which may then be examined for.

5. **Potassium dichromate** does not liberate sulphur dioxide from sulphites, but is itself reduced to green chromic sulphate. It may be used to separate sulphur dioxide and sulphuretted hydrogen from mixtures of these gases with carbon dioxide.

Sulphuric Acid.

H_2SO_4.

187. Use sodium sulphate, $Na_2SO_4 . 10H_2O$.

DRY REACTION.

Heated on charcoal with fusion mixture, a sulphide is produced (see preparation of barium chloride from barium sulphate).

$$BaSO_4 + 2C + Na_2CO_3 = Na_2S + BaCO_3 + 2CO_2.$$

The product, placed on a silver coin and moistened, produces a brown stain.

REACTION IN SOLUTION.

Barium chloride gives a heavy white precipitate of barium sulphate, insoluble in acids.

Hydrosulphuric Acid.

(Sulphuretted Hydrogen), H_2S.

188. REACTIONS. Use sodium sulphide, Na_2S.

1. Warm concentrated **hydrochloric acid** liberates sulphuretted hydrogen, which blackens lead acetate paper, from most sulphides (exceptions, mercury, silver, arsenic).

2. **Silver nitrate** gives with solutions of sulphides a black precipitate of silver sulphide, soluble in nitric acid. Solutions of other metallic salts, as those of copper, cadmium or lead, may also be used, and sulphuretted hydrogen may be separated in this way from mixtures with carbon dioxide.

Thiosulphuric Acid.

$H_2S_2O_3$.

189. DRY REACTION. Use sodium thiosulphate, $Na_2S_2O_3 . 5H_2O$.

Heated on charcoal with fusion mixture, a sulphide is produced.

REACTIONS IN SOLUTION.

1. Dilute **hydrochloric acid** decomposes thiosulphates, liberating sulphur dioxide and precipitating sulphur. (Compare sulphites.)

$$Na_2S_2O_3 + 2HCl = H_2O + 2NaCl + SO_2 + S.$$

2. **Barium chloride** gives no precipitate.

Bicarbonates when heated alone, or when boiled in water, give off water and carbon dioxide, leaving carbonates (distinction between carbonates and bicarbonates).

REACTIONS IN SOLUTION. Use a solution of sodium carbonate, $Na_2CO_3 . 10H_2O$.

1. Dilute **hydrochloric acid** liberates carbon dioxide, which may be recognised by pouring the gas into lime water. The latter is turned milky.

2. **Silver nitrate** forms a white precipitate of silver carbonate, soluble in dilute nitric acid or in ammonium hydrate.

3. **Barium chloride** produces a white precipitate of barium carbonate, soluble in dilute hydrochloric acid.

4. **Potassium dichromate** liberates carbon dioxide from carbonates or bicarbonates, but does not liberate sulphur dioxide from sulphites. The dichromate is converted into chromate, with change of colour. Compare **186**, 5.

Sulphurous Acid.

H_2SO_3.

186. Use sodium sulphite, $Na_2SO_3 . 7H_2O$.

DRY REACTION. Heated on charcoal, a sulphide is formed; when the residue is placed on a silver coin and moistened with water, a black stain is produced.

REACTIONS IN SOLUTION.

1. Dilute **hydrochloric acid** liberates sulphur dioxide, which is recognised by its smell, and by reduction of potassium dichromate solution on a strip of filter paper held in the mouth of the test-tube.

2. **Barium chloride** gives with strong solutions a white precipitate of barium sulphite, soluble in hydrochloric acid.

3. **Silver nitrate** produces a white precipitate of silver sulphite, soluble in nitric acid and in ammonium hydrate.

4. **Chlorine water** oxidises sulphites to sulphates, which may then be examined for.

5. **Potassium dichromate** does not liberate sulphur dioxide from sulphites, but is itself reduced to green chromic sulphate. It may be used to separate sulphur dioxide and sulphuretted hydrogen from mixtures of these gases with carbon dioxide.

Sulphuric Acid.

H_2SO_4.

187. Use sodium sulphate, $Na_2SO_4 . 10H_2O$.

DRY REACTION.

Heated on charcoal with fusion mixture, a sulphide is produced (see preparation of barium chloride from barium sulphate).

$$BaSO_4 + 2C + Na_2CO_3 = Na_2S + BaCO_3 + 2CO_2.$$

The product, placed on a silver coin and moistened, produces a brown stain.

REACTION IN SOLUTION.

Barium chloride gives a heavy white precipitate of barium sulphate, insoluble in acids.

Hydrosulphuric Acid.

(Sulphuretted Hydrogen), H_2S.

188. REACTIONS. Use sodium sulphide, Na_2S.

1. Warm concentrated **hydrochloric acid** liberates sulphuretted hydrogen, which blackens lead acetate paper, from most sulphides (exceptions, mercury, silver, arsenic).

2. **Silver nitrate** gives with solutions of sulphides a black precipitate of silver sulphide, soluble in nitric acid. Solutions of other metallic salts, as those of copper, cadmium or lead, may also be used, and sulphuretted hydrogen may be separated in this way from mixtures with carbon dioxide.

Thiosulphuric Acid.

$H_2S_2O_3$.

189. DRY REACTION. Use sodium thiosulphate, $Na_2S_2O_3 . 5H_2O$.

Heated on charcoal with fusion mixture, a sulphide is produced.

REACTIONS IN SOLUTION.

1. Dilute **hydrochloric acid** decomposes thiosulphates, liberating sulphur dioxide and precipitating sulphur. (Compare sulphites.)

$$Na_2S_2O_3 + 2HCl = H_2O + 2NaCl + SO_2 + S.$$

2. **Barium chloride** gives no precipitate.

3. **Silver nitrate** in excess gives a white precipitate of silver thiosulphate which on boiling turns yellow, brown, and finally black (Ag_2S).

Nitrous Acid.

HNO_2.

190. Dry Reaction. Use sodium nitrite $NaNO_2$. Heated on charcoal, nitrites deflagrate.

Reactions in Solution.

1. Dilute **hydrochloric acid** liberates brown fumes of nitrogen peroxide, together with nitric oxide.

2. A crystal or a solution of **ferrous sulphate** is turned brown when added to a solution of a nitrite, owing to the formation of the compound $2FeSO_4 . NO$.

3. **Potassium iodide** is decomposed by an acidified solution of a nitrite, liberating iodine, which gives a blue colour with starch.

4. Acidified **potassium permanganate** is decolourised, the nitrite being oxidised to nitrate.

Nitric Acid.

HNO_3.

191. Dry Reactions. Use potassium nitrate, KNO_3.

1. Heated on charcoal, nitrates deflagrate.

2. Heated in a dry tube the nitrates of the heavy metals give off nitrogen peroxide and oxygen, and leave an oxide. The nitrates of the alkali metals on strongly heating give off oxygen and leave a nitrite, and finally an oxide.

Reactions in Solution.

1. Concentrated **sulphuric acid** added to a solution of a nitrate liberates nitric acid, and on the addition of copper, brown fumes are evolved.

2. If a solution of a nitrate is mixed with an equal bulk of **ferrous sulphate** solution, and concentrated **sulphuric acid** poured carefully down the tube, so as to form a heavy layer at the bottom, a brown colouration is formed at the junction of the layers. The brown substance has the composition $2FeSO_4 . NO$, and is decomposed on warming, liberating

nitric oxide. The brown colour is thus discharged. Iodides, bromides and nitrites interfere with this test.

Detection of Nitrates in presence of Bromides and Iodides.

Dissolve in the solution of the nitrate a crystal of potassium iodide, add a little starch paste, a small quantity of dilute sulphuric acid and a piece of zinc. The zinc liberates hydrogen, which reduces the nitrate to nitrite, and this in turn liberates iodine, which produces a blue colour with the starch paste.

If nitrites are already present, they must be removed before applying the above test. This may be done by boiling for a few minutes with ammonium chloride.

Chromic Acid.

H_2CrO_4.

Permanganic Acid.

$H_2Mn_2O_8$.

The reactions of these acids will be found among those of the metals, under chromium and manganese respectively (pars. **161** and **165**).

Phosphoric Acid.

H_3PO_4.

192. Use sodium phosphate, $Na_2HPO_4 . 12H_2O$.

Dry Reaction.

Heated on charcoal, moistened with cobalt nitrate and reheated, phosphates give a blue mass.

Reactions in Solution.

1. **Silver nitrate** produces a canary yellow precipitate of silver phosphate, Ag_3PO_4, soluble in nitric acid or in ammonium hydrate.

2. **Barium chloride** gives a white precipitate of barium phosphate, $BaHPO_4$, soluble in acetic acid.

3. **Ammonium molybdate** when added to a solution of a phosphate in the presence of strong nitric acid produces a yellow precipitate of ammonium phosphomolybdate either at once or on very gently warming. (Compare arsenates, **156.**)

4. **Magnesia mixture** forms a white precipitate of magnesium ammonium phosphate, $MgNH_4PO_4 . 6H_2O$, soluble in acids. (Compare arsenates, **156**.)

5. **Ferric chloride** gives a yellowish white precipitate of ferric phosphate, $FePO_4$, soluble in excess of ferric chloride, insoluble in acetic acid. If the hydrochloric acid produced in the reaction is removed (by addition of sodium acetate) all the iron is precipitated.

Arsenious Acid.

H_3AsO_3.

Arsenic Acid.

H_3AsO_4.

The reactions of these two acids will be found among those of the metals (par. **156**).

Boric Acid.

H_3BO_3.

193. Dry Reactions. Use borax, $Na_2B_4O_7 . 10H_2O$.

1. Borates when heated swell up, fuse, and leave a transparent mass which, when moistened with cobalt nitrate and reheated, gives a blue colour.

2. Place a little of the borate in a porcelain dish, add a few drops of strong **sulphuric acid** and a little **methylated spirit**, stir and apply a flame to the mixture. A green flame is obtained.

3. The above test is better carried out by heating a small quantity of the borate, mixed with **calcium fluoride** and potassium hydrogen sulphate and made into a stiff paste with water, on a platinum wire. Boron fluoride is liberated, which colours the flame green.

$$CaF_2 + 2KHSO_4 = CaSO_4 + K_2SO_4 + 2HF.$$
$$B_2O_3 + 6HF = 3H_2O + 2BF_3.$$

4. Boric acid (liberated from a borate by addition of an acid) gives a brown stain on **turmeric** paper. The stain becomes greenish black on addition of an alkali.

Reaction in Solution.

Silver nitrate gives a white precipitate of metaborate,

soluble in ammonium hydrate and in nitric acid. On boiling, the precipitate turns brown and finally black owing to reduction.

Silicic Acid.

H_2SiO_3.

194. DRY REACTIONS. Use sodium silicate, Na_2SiO_3.

1. Heated on charcoal, moistened with cobalt nitrate and reheated, silica and silicates give a blue mass on fusion (compare aluminium, **162**, 1).

2. Mixed with a **fluoride** and heated with concentrated **sulphuric acid**, silicon tetrafluoride is produced (see fluorides, **182**, 2). This test must not be carried out in a glass vessel.

3. Heated in a **microcosmic** bead, *silica does not dissolve*, and silicates only very slowly.

4. Heated with **sodium carbonate**, soluble silicates are produced.

REACTIONS IN SOLUTION. Use soluble glass, Na_2SiO_3.

1. **Hydrochloric acid** liberates the silicic acid, which remains in solution in a colloidal state. On evaporation to dryness, insoluble silica is produced.

2. **Ammonium carbonate** gives a precipitate of silicic acid on boiling, ammonia being evolved.

3. **Silver nitrate** produces orange-coloured silver silicate, Ag_2SiO_3, which is soluble in ammonium hydrate and nitric acid.

Hydrogen Peroxide.

H_2O_2.

195. REACTIONS.

1. Hydrogen peroxide decomposes on heating, especially in presence of alkalies, oxygen being evolved.

2. To a solution of hydrogen peroxide (or sodium peroxide dissolved in water, using proper precautions) add dilute **sulphuric acid,** a little **ether,** and one or two drops of potassium **dichromate** solution, and shake. A deep blue colour is given to the layer of ether.

3. **Potassium iodide** added to an acidified solution of the peroxide yields iodine.

4. **Potassium permanganate**, acidified with sulphuric acid, is at once decolourised by hydrogen peroxide, oxygen being evolved from both substances.

Metallic Oxides and Hydroxides.

196. The oxides of heavy metals are practically insoluble in water, and are variously coloured. Those of zinc and aluminium are colourless, zinc oxide becoming yellow on heating. Most of them dissolve readily in hydrochloric acid.

The oxides of the alkaline earth metals are colourless, and unite with water, with evolution of heat, to form soluble hydroxides, the solutions having an alkaline reaction. Magnesium oxide does not combine with water, but is very sparingly soluble, and faintly alkaline in reaction.

Oxides of the alkali metals also unite with water, with evolution of heat, forming the caustic alkali hydroxides. These in the solid form are deliquescent, and absorb carbon dioxide from air.

Hydroxides of heavy metals give up water on heating, and in general leave anhydrous oxides.

Peroxides of the heavy metals in general evolve a portion of the oxygen on heating alone, or with sulphuric acid, and liberate chlorine when heated with strong hydrochloric acid, *e.g.* red lead, manganese dioxide.

ORGANIC ACIDS.

The reactions of some of the commoner organic acids will be found in Part I. B. See Index.

Hydrocyanic Acid.

HCN.

197. Cyanides of the alkali metals are readily soluble in water, those of the alkaline earths sparingly soluble, the solutions being alkaline in reaction. Those of the heavy metals, except mercuric cyanide, $Hg(CN)_2$, are insoluble in water, but generally soluble in solution of potassium cyanide. Most cyanides are decomposed by dilute acids, evolving hydrocyanic acid.

When heated alone, most heavy metal cyanides decompose, evolving the poisonous, combustible cyanogen gas. The alkali cyanides fuse on heating, and oxidise in air to cyanates. Heated with sulphur, potassium cyanide forms thiocyanate, KSCN, which produces a blood-red colour with ferric chloride. Hence the use of potassium cyanide as a reducing agent for oxides and sulphides.

REACTIONS IN SOLUTION. Use a solution of potassium cyanide.

1. **Silver nitrate** gives a white curdy precipitate of silver cyanide, AgCy, which dissolves until one molecule of silver nitrate has been added for each two molecules of potassium cyanide, forming the compound AgCy . KCy. The addition of more $AgNO_3$ produces a permanent precipitate of AgCy, which greatly resembles AgCl, being soluble in AmOH, $Na_2S_2O_3$, etc., and insoluble in dilute HNO_3. To distinguish and separate silver cyanide from the halide salts, ignite the dry precipitate; the cyanide decomposes, leaving metallic silver, which may be dissolved by strong HNO_3; the halide salts fuse without decomposition, and AgCl may then be extracted with strong AmOH.

2. Free HCN, liberated from KCN with a little dilute acid in a small beaker, decomposes yellow **ammonium sulphide** placed on the bottom of a watch-glass over the beaker, forming thiocyanate.

$$Am_2S_2 + HCN = AmSCN + AmHS.$$

This, when acidified with HCl to decompose the hydrosulphide, gives a deep-red colour with $FeCl_3$. This is a very delicate test for hydrocyanic acid.

3. To the solution of cyanide add a mixture of $FeSO_4$ and $FeCl_3$ solutions, and acidify with HCl to dissolve hydroxides of iron. A deep-blue precipitate, or a blue or green colouration of **Prussian blue**, is obtained. (See Ferrocyanic Acid, 199.)

Thiocyanic Acid.

HSCN.

198. REACTIONS IN SOLUTION. Use a solution of potassium or ammonium thiocyanate.

1. **Silver nitrate** produces a white curdy precipitate of silver thiocyanate, AgSCN, insoluble in dilute acids, soluble in AmOH.

2. **Copper sulphate**, to which sulphurous acid has been added, forms a white precipitate of cuprous thiocyanate, $Cu_2(SCN)_2$. On ignition this leaves cuprous sulphide, Cu_2S, and is employed as a means of estimating copper.

3. **Ferric chloride** solution gives a deep-red colouration, owing to the formation of the soluble ferric thiocyanate, $Fe(SCN)_3$. Ferrous salts give no colour.

Hydroferrocyanic Acid.

H_4FeCy_6.

199. Use potassium ferrocyanide, $K_4FeCy_6 . 3H_2O$.

DRY REACTIONS.

1. Heated alone, potassium ferrocyanide decomposes into cyanide, nitrogen and a carbide of iron:

$$K_4FeCy_6 = 4KCy + N_2 + FeC_2 (\text{or } Fe + 2C).$$

2. Heated with concentrated sulphuric acid, carbon monoxide is evolved (see preparation of this, **35**, 3).

REACTIONS IN SOLUTION.

1. **Silver nitrate** precipitates white silver ferrocyanide, Ag_4FeCy_6, insoluble in dilute acids or AmOH, soluble in potassium cyanide.

2. **Copper sulphate** produces a brown (CuK_2FeCy_6) or chocolate (Cu_2FeCy_6) precipitate, according to the proportions employed.

3. **Ferrous salts** give a white precipitate of potassium ferrous ferrocyanide, which is quickly oxidised to the blue ferric salt:

$$3FeSO_4 + 2K_4FeCy_6 = Fe_3K_2(FeCy_6)_2 + 3K_2SO_4.$$

Owing to this oxidation the usual precipitate is of a light-blue colour.

4. **Ferric salts** give a dark-blue precipitate of Prussian blue, ferric ferrocyanide,

$$4FeCl_3 + 3K_4FeCy_6 = Fe_4(FeCy_6)_3 + 12KCl.$$

These precipitates are insoluble in dilute acids, but are

decomposed by caustic alkalies, forming the alkali ferrocyanide and ferrous or ferric hydroxide.

$$Fe_3K_2(FeCy_6)_2 + 6KOH = 2K_4FeCy_6 + 3Fe(OH)_2.$$
$$Fe_4(FeCy_6)_3 + 12KOH = 3K_4FeCy_6 + 4Fe(OH)_3.$$

Hydroferricyanic Acid.

H_3FeCy_6.

200. REACTIONS IN SOLUTION. Use potassium ferricyanide, K_3FeCy_6.

1. **Silver nitrate** precipitates orange-coloured silver ferricyanide, Ag_3FeCy_6, insoluble in dilute HNO_3, soluble in AmOH or KCy solution.

2. **Ferrous salts** give a dark-blue precipitate of ferrous ferricyanide (Turnbull's blue).

$$3FeSO_4 + 2K_3FeCy_6 = Fe_3(FeCy_6)_2 + 3K_2SO_4.$$

This is insoluble in water or dilute acids, but is decomposed by caustic alkalies, into alkali ferricyanide and ferrous hydroxide.

$$Fe_3(FeCy_6)_2 + 6KOH = 2K_3FeCy_6 + 3Fe(OH)_2.$$

The ferricyanide rapidly changes to ferrocyanide, while the iron hydroxide is oxidised.

3. **Ferric salts** give only a brown colouration.

201. Table of Solubilities.

1 = Soluble in water.

2 = Sparingly soluble in water; soluble in dilute acids.

	K	Na	Li	NH_4	Mg	Ca	Sr	Ba	Fe ous	Fe ic	Cr	Al	Zn
Cl	1	1	1	1	1	1	1	1	1	1	1	1	1
Br	1	1	1	1	1	1	1	1	1	1	1	1	1
I	1	1	1	1	1	1	1	1	1	1	1	1	1
Fl	1	1	1	1	4	4	4	4	2	1	1	1	2
Cl_2O					All hypochlorites are soluble in water.								
Cl_2O_5					All chlorates are soluble in water.								
CN	1	1	1	1	1	1	1	2	4	–	3	–	3
Cfo[4]	1	1	1	1	1	1	1	2	4	4	–	–	4
Cfi[4]	1	1	1	1	1	1	–	–	4	1	–	–	4
O	1	1	1	1	3	2	2	1	3	3	3	3	3
S	1	1	1	1	1	1	1	1	3	3	3	3	3
SO_2	1	1	1	1	1					All other sulphites			
SO_3	1	1	1	1	1	4	4	5	1	1	1	1	1
S_2O_3	1	1	1	1	1	1	1	2	1	1	1	1	1
CO_2	1	1	2	1	3	3	3	2	All other carbonates				
SiO_2	1	1	1	–			All other silicates solubility 3.						
N_2O_3							All nitrites soluble in water.						
N_2O_5							All nitrates soluble in water.						
P_2O_5	1	1	2	1			All other phosphates soluble in						
As_2O_3	1	1	1	1			All other arsenites soluble in						
As_2O_5	1	1	1	1			All other arsenates soluble in						
B_2O_3	1	1	1	1			All other borates soluble in						
CrO_3	1	1	1	1	1	2	2	3	–	1	3	–	1
Mn_2O_7					All other permanganates are soluble in water.								
$(C_2H_3O_2)$[5]					All acetates soluble in water.								
(C_2O_4)	1	1	1	1	All other oxalates solubility 2.								
$(C_4H_4O_6)$	1	1	1	1	2	2	2	2	1	1	1	1	2

[1] Readily soluble in hot water.

[2] Decomposed by water into basic compounds of solubility 3.

[3] Soluble only in aqua regia.

3 = Insoluble in water; soluble in acids.
4 = Insoluble in water; difficultly soluble in acids.
5 = Insoluble in water or acids.

Mn	Ni	Co	Sb	Sn ous	Sn ic	Pb	Hg ous	Hg ic	Ag	Bi	Cu	[illegible]	
1	1	1	1[2]	1	1	1[1]	4	1	5	1[2]	1	1	Cl
1	1	1	1[2]	–	–	1[1]	3	1	5	2	1	1	Br
1	1	1	2	1	1	1[1]	2	2	5	3	1	1	I
3	2	2	1	1	1	3	–	2	1	1	3	2	Fl
													Cl_2O
													Cl_2O_5
3	4	4	–	–	–	3	–	1	5	–	4	3	CN
3	5	5	–	–	5	3	–	–	5	–	5	–	Cfo[4]
3	5	5	–	–	–	2	–	–	5	–	–	–	Cfi[4]
3	3	3	3	3	4	3	3	3	3	3	3	3	O
3	3[3]	3[3]	3	3	3	3	–	3[3]	3	3	3	3	S
soluble in acids.													SO_2
1	1	1	3	1	–	4	2	1	2	1	1	1	SO_3
1	1	1	1	1	1	2	1	1	2	1	1	1	S_2O_3
solubility 3.													CO_2
													SiO_2
													N_2O_3
													N_2O_5
acids.													P_2O_5
acids.													As_2O_3
acids.													As_2O_5
acids.													B_2O_3
1	3	3	–	–	–	4	3	2	3	3	1	1	CrO_3
									2				Mn_2O_7
													$(C_2H_3O_2)$[5]
													(C_2O_4)
2	1	1	1	1	1	2	2	2	2	1	2	2	$(C_4H_4O_6)$

[4] Hydroferro- and hydroferricyanic acids.
[5] Fe, Al, Pb, Cu also form basic acetates, solubility 2.

A METHOD OF ANALYSIS.

202. Preliminary Examination.

The substance should be carefully described before proceeding with the tests.

EXPERIMENT.	OBSERVATION.	INFERENCE.
Heat a little of the substance in a dry tube	Fusion	Salts of the alkalies and some salts of Ba, Sr, and Ca. Also salts containing water of crystallisation.
	A colourless liquid condenses in the cooler portions of the tube	Salts containing water of crystallisation.
	The liquid is alkaline	NH_4.
	The liquid is acid	Acid salts.
	A gas is evolved:	
	oxygen	Some oxides; nitrates, chlorates, etc.
	ammonia	NH_4.
	sulphur dioxide	Sulphites or sulphates of heavy metals.
	sulphuretted hydrogen	Some sulphides in presence of water.
	nitrogen peroxide (brown)	Nitrates of heavy metals.
	bromine (brown)	Bromides, in presence of oxidising agents.
	chlorine	Chlorides, etc., some chlorates and hypochlorites.
	iodine	Iodides or free iodine
	carbon dioxide	Carbonates of heavy metals, bicarbonates, oxalates, etc.
	cyanogen	Some cyanides.
	A sublimate is formed:	
	white	NH_4, Hg, As.

Experiment.	Observation.	Inference.
	white, with irritating fumes	Oxalic acid, etc.
	yellow	As_2S_3, HgI_2 (red when rubbed).
	yellow (which melts on heating)	Free S, or from thiosulphates or sulphides.
	metallic mirror (small beads)	Hg.
	dark grey	As, Sb.
	The residue is	
	white, infusible	Ba, Sr, Ca, Zn, Al, Mg, etc.
	white, yellow hot	ZnO.
	yellow, fusible, reddish brown hot	PbO, Bi_2O_3.
	reddish brown, black hot	Fe_2O_3.
	brown	Mn_3O_4.
	black	CuO, Co_3O_4, NiO.
	charred	Organic matter.
Heat a little of the substance on charcoal in the blowpipe flame.	Decrepitation	NaCl, $Pb(NO_3)_2$, etc.
	Deflagration	Nitrates, nitrites, chlorates.
	A bead *of metal* is produced:	
	greyish white, malleable, soft, marks paper	Pb.
	white (red tinge), brittle	Bi.
	white, hard	Ag.
	An incrustation is formed:	
	white	Sb, NH_4.
	white (fumes with garlic odour)	As.
	white, yellow hot	Zn, Sn.
	yellow	Bi.

Experiment.	Observation.	Inference.
	The residue is	
	fusible	Salts of alkalies, etc.
	white, infusible	Mg, Ba, Sr, Ca, Zn, Al.
	coloured	Cu, Fe, Cr, Co, Ni, etc.
If the residue is white, moisten with a few drops of $Co(NO_3)_2$ and re-heat.	blue mass	Al (possibly phosphates, silicates, etc.).
	green mass	Zn.
	pink mass (difficult)	Mg.
Heat a little of the substance on platinum wire.	The flame is	
	bright yellow	Na.
	lambent blue	Pb, Cu, Sb, As, Bi, Cd, Zn.
	green	Cu, B_2O_3, Ba.
	dull red	Ca.
	crimson	Sr, Li.
	lilac	K.

	Observation.		Inference.
If the residue on charcoal is not white, heat a little of the substance in a borax bead.	The bead is in the		
	Oxidising flame	*Reducing flame*	
	reddish brown	colourless	Mn.
	reddish brown	grey	Ni.
	greenish blue	red	Cu.
	yellow, red when hot	yellow (hot) bottle-green (cold)	Fe.
	green	green	Cr.
	blue	blue	Co.
Grind a little of the substance in a mortar with soda lime.	Ammonia is evolved		NH_4.

FINAL EXAMINATION FOR BASIC RADICALS.

203. Preparation of a solution.

(If the substance is a liquid it should be examined by (*a*) testing with litmus, (*b*) evaporating a little to dryness to see whether solids are present, (*c*) heating the residue, if any, to see whether organic substances are present.)

Take a *small* quantity of the substance, add water and boil.

If the substance is soluble in water, note its action on litmus, and proceed with the separation into groups.

If it does not dissolve, test the liquid with litmus paper; if alkaline or acid, a portion has dissolved. If neutral to litmus, filter a few drops and evaporate to see whether a part has dissolved. Now add a little dilute hydrochloric acid to the substance and boil for a few minutes. If a residue is left, boil further, add more water and boil again.

If the substance is found to be insoluble in dilute hydrochloric acid, boil a fresh quantity with strong hydrochloric acid for several minutes, add water and boil.

If not entirely soluble, boil another portion with aqua regia, evaporate nearly to dryness, add a little strong hydrochloric acid and evaporate to a small bulk to remove nitric acid. Dilute with water.

If yet some or all remains undissolved, warm a little with nitric acid, and if soluble add hydrochloric acid. A white precipitate, if formed, should be tested for the silver group and the hydrochloric acid (or aqua regia) solution proceeded with for the other groups.

If insoluble after the above treatment, examine by the method for insolubles, par. 214.

In many cases it will be advantageous to treat the water or hydrochloric acid extract separately from that obtained by aqua regia, as the number of substances insoluble in hydrochloric acid but soluble in aqua regia is very limited, and those may often be easily identified.

204. Separation of the Metals into Groups.

To the cold solution add a few drops of HCl (if the substance has been dissolved in HCl this is unnecessary). If a precipitate is produced add more acid till there is no further precipitate.

Precipitate: May consist of
$AuCl_3$ (white)
AgCl (white)
HgCl (white)
Examine by table for the **silver** group.

Solution: Pass H_2S till no further precipitate, and warm. Filter, dilute the filtrate, and if a further precipitate is produced, pass more H_2S. (If an arsenate is suspected, add sulphurous acid, boil off excess, and pass H_2S.)

Precipitate: May consist of
HgS (yellow, finally black)
PbS (black, may be red)
CuS (dark brown)
Bi_2S_3 (black)
CdS (yellow)
As_2S_3 (yellow)
Sb_2S_3 (orange red)
SnS (dark brown)
SnS_2 (yellow)
S (very pale yellow)
Solution changes colour:
from yellow to green, chromates;
from yellow to pale green or colourless, ferric salts.
In both cases sulphur is precipitated.
Examine by table for **copper** group.

Solution: Boil off H_2S, concentrating the liquid if bulky. Add 2 or 3 drops of strong HNO_3 and boil. Take a little of the solution and test for phosphates by ammonium molydate test. To the remainder of the solution add NH_4Cl, boil, add slight excess of ammonium hydrate, boil, and filter immediately. (The precipitate may be due to organic substances, silicates, etc. If these are present, they should be eliminated after passage of H_2S, by evaporating to dryness and igniting.)

Precipitate: If phosphates are absent, may consist of
$Fe(OH)_3$ (reddish brown)
$Cr(OH)_3$ (green)
$Al(OH)_3$ (white)
If phosphates are present, all the metals of the iron, zinc and barium groups and magnesium may be precipitated as phosphates together with the above hydrates.
Examine by table for **iron** group, or by the **phosphate** table.

Solution: At once pass H_2S.

Precipitate: May consist of
CoS (black)
NiS (black)
MnS (flesh coloured)
ZnS (white)
Examine by table for **zinc** group.

Solution: Add NH_4OH till the liquid smells of NH_3, then $(NH_4)_2CO_3$ till no further precipitate; warm (do not boil) and allow to stand for ten minutes.

Precipitate: May consist of
$BaCO_3$ (white)
$SrCO_3$ (white)
$CaCO_3$ (white)
Examine by table for **barium** group.

Solution: May contain the metals Mg, K, Na, Li.
Examine by table for **sodium** group

205. Separation of the Metals of the Silver Group.

Wash the precipitate with cold water; then pour on boiling water, collecting the hot filtrate.

Solution: May contain $PbCl_2$.	*Residue*: Pour over it a small quantity of NH_4OH.	
Allow to cool; white needle-shaped crystals separate,	*Solution*: Acidify with HNO_3; white precipitate.	*Residue*: Black (NH_2Hg_2Cl).
Pb is present.	**Ag** is present.	**Hg** is present.
If no precipitate on cooling, add K_2CrO_4; yellow precipitate of $PbCrO_4$.		Dissolve in small quantity of aqua regia, dilute largely and place in the solution a clean strip of copper.
		Grey deposit of mercury.

206. Separation of the Metals of the Copper Group.

Wash well with hot water, transfer to a test-tube and boil with yellow ammonium sulphide (if tin and mercury are absent, sodium hydrate may be used). Filter.

<table>
<tr><td colspan="4">Residue: Wash well, transfer to a test-tube, add a little strong HNO_3, heat till red fumes cease, dilute. Test a few drops for lead with dilute H_2SO_4 and alcohol. If lead is present mix the whole of the liquid with H_2SO_4 (a few drops) and alcohol (an equal bulk), and allow to stand for 10 minutes in the cold.</td><td colspan="3">Solution: Acidify with dilute HCl; a precipitate shows the presence of As, Sb, or Sn. Boil the moist precipitate with strong HCl and filter.</td></tr>
<tr><td colspan="2">Residue: If lead is present, warm with ammonium acetate.</td><td colspan="2">Solution: If alcohol has been added, boil this off, add excess of NH_4OH and warm;</td><td rowspan="2">Residue: May consist of As_2S_3 or S.

Dissolve in a small quantity of aqua regia, dilute largely and apply Reinsch's test.

Grey deposit,

As is present.</td><td colspan="2">Solution: Make just alkaline with ammonia, add a few grams of oxalic acid and boil. Pass H_2S;</td></tr>
<tr><td>Residue: Dissolve in a little aqua regia, dilute and place in the solution a bright strip of copper. Grey deposit, which becomes bright on rubbing,

Hg is present.</td><td>Solution: Add K_2CrO_4. Yellow precipitate,

Pb is present.</td><td>Precipitate: Pour over it a few drops of dilute HCl and dilute the liquid largely with water; white precipitate,

Bi is present.</td><td>Solution: If colourless, Cu is absent; pass H_2S, yellow precipitate—Cd is present.
If blue, Cu is present; divide the solution into two parts.
To one part add acetic acid in excess and $K_4Fe(CN)_6$; brown precipitate, Cu is present.
To the other part add KCN till colourless and pass H_2S; yellow precipitate,
Cd is present.</td><td>Precipitate: Orange coloured,

Sb is present.</td><td>Solution: Neutralise with ammonium hydrate, acidify with acetic acid, boil and pass H_2S; brownish yellow precipitate,

Sn is present.</td></tr>
</table>

207. Separation of the Metals of the Iron Group (Phosphates being absent).

Wash well, pour a little warm dilute HCl over the precipitate several times to dissolve the hydrates; to this solution add excess of NaOH, boil and filter.

Precipitate: Place on a piece of platinum foil, cover with fusion mixture and a little KNO_3 and fuse. Boil the residue with water; filter.		*Solution*: Add 2 or 3 drops of litmus solution, acidify with HCl and add NH_4OH till alkaline: White precipitate which forms a "lake" with the colouring matter; **Al** is present.
Residue: reddish brown, **Fe** is present. Dissolve in HCl, and add $K_4Fe(CN)_6$; Dark blue precipitate.	*Solution*: Yellow, **Cr** is present. Add acetic acid in excess, and lead acetate, Yellow precipitate.	

207a. Alternative Method (Phosphates absent).

Wash well, pour a little warm dilute HCl over the precipitate several times to dissolve the hydrates; to this solution add sodium peroxide carefully, in small quantities, until in excess, boil and filter.

Precipitate: Reddish brown, **Fe** is present. Confirm as above.	Solution may contain sodium chromate and aluminate. Divide into two parts.	
	(1) Yellow solution, **Cr** is present. Add acetic acid in excess, and lead acetate; Yellow precipitate.	(2) Test for aluminium as described above.

208. Separation of the Metals precipitated in the Iron Group (Phosphates being present).

Wash well, dissolve in the smallest possible quantity of dilute HCl, nearly neutralise with solid sodium carbonate, and add an equal bulk of sodium acetate and acetic acid. If the solution is red, there is more iron than is sufficient to precipitate all the phosphoric acid. Boil till all the ferric acetate is precipitated, *i.e.* until the liquid is colourless. If the solution is colourless, boil and filter at once.

<table>
<tr>
<td rowspan="5">Precipitate: May consist of phosphates and basic acetates of Fe, Al, and possibly some of the Cr.
Examine by table for iron group, the phosphates of these metals behaving like the hydrates.</td>
<td colspan="5">Solution: If the solution was red, no phosphoric acid remains; proceed with the separation into groups by NH_4Cl, NH_4OH, etc. If the solution was colourless, phosphoric acid may yet be present. Test 2 or 3 drops by adding one drop of dilute $FeCl_3$ solution; if a red colour is produced, proceed with the separation. If no red colour is produced, add $FeCl_3$ to the whole solution drop by drop till no further precipitate is formed. Boil to precipitate the ferric acetate, i.e. till the liquid is colourless. Filter.</td>
</tr>
<tr>
<td rowspan="4">Precipitate: Is ferric phosphate and basic acetate.
Neglect.</td>
<td colspan="4">Solution: Add NH_4Cl, boil, add NH_4OH, boil and filter.</td>
</tr>
<tr>
<td rowspan="3">Precipitate: May consist of aluminium and chromium hydrates.
Examine by portion of table for iron group.</td>
<td colspan="3">Solution: Pass H_2S while still warm.</td>
</tr>
<tr>
<td rowspan="2">Precipitate: May consist of CoS, NiS, MnS, ZnS.
Examine by table for zinc group.</td>
<td colspan="2">Solution: Add NH_4OH and $(NH_4)_2CO_3$ and warm.</td>
</tr>
<tr>
<td>Precipitate: May consist of $BaCO_3$, $SrCO_3$, $CaCO_3$.
Examine by table for barium group.</td>
<td>Solution: May contain magnesium. Add Na_2HPO_4:
White precipitate on standing.
Mg is present.</td>
</tr>
</table>

209. Separation of the Metals in the Zinc Group.

If the precipitate is not black, it may be dissolved in warm dilute HCl and tested for Mn and Zn only.

If black, wash the precipitate into a small porcelain dish with very dilute hydrochloric acid (1 of acid to 5 of water), stir till no more H_2S is evolved.

<table>
<tr>
<td rowspan="2">Residue: Test in borax bead. If the bead is brown, Co is absent, Ni is present.

If the bead is blue, wash the residue into a small porcelain dish, add a little strong HCl and a crystal of $KClO_3$, and heat till dissolved. Evaporate the solution just to dryness and dissolve in a little water. Nearly neutralise with sodium carbonate (solid may be used to avoid increase of bulk), and add KCN till the precipitate at first formed just re-dissolves. Boil for 5 minutes in the fume cupboard. Now add 5 or 6 drops of NaOH and bromine water till the solution is just coloured.

Warm; a black precipitate, Ni is present.

Wash the precipitate and confirm by borax bead.

Evaporate the solution to dryness and test in borax bead; blue bead, Co is present.</td>
<td colspan="2">Solution: Boil till free from H_2S, add NaOH in excess, boil and filter.</td>
</tr>
<tr>
<td>Residue: is $Mn(OH)_2$.

Confirm by bead of sodium carbonate with a crystal of KNO_3; green bead,

Mn is present.</td>
<td>Solution: Pass H_2S; white precipitate,

Zn is present.</td>
</tr>
</table>

210. Separation of the Metals of the Barium Group.

Pour warm dilute acetic acid over the precipitate on the filter paper several times to dissolve the carbonates; add K_2CrO_4.

<table>
<tr>
<td rowspan="2">Precipitate: yellow.

Ba is present.

Wash and test on platinum wire; green flame.

Dissolve in dilute HCl and add H_2SO_4.

White precipitate of $BaSO_4$, insoluble even on boiling.</td>
<td colspan="2">Solution: Add $(NH_4)_2SO_4$; warm and allow the solution to stand ten minutes.</td>
</tr>
<tr>
<td>Precipitate: white.

Sr is present.

Wash and test on platinum wire; crimson flame.

Ca may be precipitated here if the solution is strong, but may be removed by dissolving in a warm concentrated solution of ammonium sulphate.</td>
<td>Solution: Add ammonium oxalate; white crystalline precipitate.

Ca is present.</td>
</tr>
</table>

211. Separation of the Metals of the Sodium Group.

Divide the solution into two parts.

Smaller part: Add Na_2HPO_4 and allow to stand; white crystalline precipitate. **Mg** is present. Filter, add NaOH to filtrate and boil; white precipitate of Li_3PO_4. **Li** is present. Confirm by the flame-test with the precipitate.	*Larger part*: Evaporate to dryness in a small porcelain dish, and heat strongly on platinum foil, to drive off the ammonium compounds. If no residue, K, Na, Mg and Li are absent. If a residue, test on platinum wire; yellow flame, **Na** is present; lilac flame, **K** is present; crimson flame, **Li** is present. The flame of K may be identified in presence of the Na flame by using a blue glass or prism. If Na is present, K should always be tested for by $PtCl_4$. To do this, dissolve the residue in the smallest possible quantity of water, place on a watch-glass, add $PtCl_4$ and rub gently with a glass rod; heavy yellow precipitate. **K** is present.

212. Preliminary Examination for Acid Radicals.

Experiment.	Observation.	Inference.
Warm a little of the substance with dilute HCl.	Effervescence (gas evolved):	
	CO_2 (tested with lime water)	Carbonates.
	SO_2	Sulphites.
	SO_2 and S precipitated	Thiosulphates.
	H_2S	Sulphides.
	red fumes	Nitrites.
	chlorine	Hypochlorites.
	HCN	Cyanides.
Warm a little of the substance with strong H_2SO_4.	Acid fumes (test for HCl by adding MnO_2):	Chlorides, nitrates, fluorides.
	odour of acetic acid	Acetates.
	Cl_2	Chlorides in presence of an oxidising agent.
	CO_2	Carbonates, oxalates, etc.
	CO	Oxalates, formates, ferrocyanides, etc.
	chromyl chloride (red)	Chlorides in presence of chromates.
	red fumes	Nitrites or bromides.
	red fumes in presence of chlorine (bleaches)	Nitrates in presence of chlorides.
	violet fumes	Iodine or iodides.
	crackling in tube, and greenish yellow gas	Chlorates.
	SO_2	Sulphites or substances which reduce the H_2SO_4.
	H_2S	Sulphides or reducing agents.
	S	Reduction of H_2SO_4.
	charring, with evolution of SO_2 and CO_2	Tartrates, etc.
	greasy appearance in the tube	Fluorides.

By these preliminary tests for acids, many have been definitely shown to be either present or absent. Phosphates have been tested for in the separation of the metals into groups, and the presence or absence of other acids is shown by the metals found, and the solubility of the substance (*e.g.* a sulphate cannot be present in a substance which is soluble in water or acids, if barium be present). A final examination for acids must now be made.

213. Final Examination for Acid Radicals.

Prepare a neutral solution of the substance, which will contain the acids as soluble salts of sodium, as follows:—Boil a little of the substance for several minutes with a strong solution of sodium carbonate, filter, and *neutralise* the filtrate by adding HNO_3 in slight excess, boiling to expel CO_2, then adding AmOH in very slight excess, and boiling until quite neutral.

To a portion of this solution add $AgNO_3$.	A precipitate is obtained which is insoluble in HNO_3 and	
	white (sol. in NH_4OH)	HCl, $H_4Fe(CN)_6$, HCN.
	pale yellow (sol. in NH_4OH)	HBr.
	yellow (insol. in NH_4OH)	HI.
	orange yellow (sol. in NH_4OH)	$H_3Fe(CN)_6$.
	The precipitate is soluble in HNO_3, and is	
	white	HNO_2, H_2SO_3, H_2CO_3, H_3BO_3.
	black	H_2S.
	yellow	H_3PO_4, H_3AsO_3.
	orange	H_2SiO_3.
	brown	$H_2S_2O_3$.
	chocolate	H_3AsO_4.
	red	H_2CrO_4.

To another portion add $BaCl_2$	The precipitate is insoluble in HCl, and is white	H_2SO_4, HF.
	The precipitate is soluble in HCl, and is white	H_3PO_4, $H_2S_2O_3$, H_3BO_3, H_3AsO_3, H_3AsO_4, H_2SiO_3, H_2SO_3, H_2CO_3.
	yellow	H_2CrO_4.

In most cases the preparation of a neutral solution is a waste of time, and the $AgNO_3$ and $BaCl_2$ reactions may be carried out in nitric acid and hydrochloric acid solutions respectively. It will be seen from the previous table that substances other than those precipitated by the reagents in acid solutions, have already been tested for in the preliminary examination for acids or separation of metals, or need confirmation by tests which alone establish their presence. Hence, unless the metals present interfere with the detection of certain acids, it is best to omit the preparation of this neutral solution.

The student should now write down a list of acids still to be tested for or confirmed, *e.g.* HNO_3, H_3BO_3 etc., and take each separately. For HNO_3, this in presence of HBr or HNO_2, H_3BO_3, HF, and HCl, HBr, HI together, confirmatory tests will be found among the reactions of these acids.

The properties of the substance should now be compared with those of the possible compounds of the bases and acids found. It may thus be possible to decide not only the radicals, but the compounds themselves which are present in the given substance.

214. Treatment of the Insoluble Portion.

The insoluble substances include the following: SiO_2 and silicates, $BaSO_4$, $SrSO_4$, AgCl, AgBr, AgI, SnO_2, Sb_2O_4, As_2S_3, CaF_2, and Fe_2O_3, Cr_2O_3, Al_2O_3 after intense ignition. Wash the insoluble residue well with hot water.

If the original substance has been treated with aqua regia, any silver bromide or iodide will now be changed to chloride;

therefore if the residue be washed with ammonia this will be removed and may be reprecipitated by nitric acid.

If silver is found, take a little of the original substance, add H_2SO_4 and zinc, and leave in contact with the substance for 20 minutes. The silver will have been replaced by zinc, and the soluble zinc salts may now be tested for chloride, bromide and iodide.

Having removed the silver, fuse the residue on platinum foil with fusion mixture, and boil the product with water. Filter, and wash well.

<table>
<tr>
<td colspan="2">Residue: May contain Fe_2O_3 (brown), $BaCO_3$, $SrCO_3$, and any unaltered SnO_2, CaF_2, etc. Boil with HCl.</td>
<td colspan="2">Solution: May contain silicate, aluminate, chromate (yellow), stannate, antimonate, arsenate, sulphate, and fluoride of sodium in addition to the Na_2CO_3 and K_2CO_3 of the fusion mixture. Divide into a large and a small portion.</td>
</tr>
<tr>
<td>Residue: Brown, Fe_2O_3. Confirm by borax bead.</td>
<td>Solution: Examine for Ba and Sr.</td>
<td>SMALL PART.
Test for H_2SO_4.
Test for silica and silicates by heating a small portion of the insoluble residue in microcosmic bead or by CaF_2 and H_2SO_4. (See tests for silicates.)</td>
<td>LARGE PART.
Examine for metals by separation into groups, etc., removing the silica by evaporation to dryness after the removal of the copper group.</td>
</tr>
</table>

Detection of Organic Acids.

215. If these are present they must be specially examined for, in a solution containing only the salts of alkali metals. To prepare this, boil the original substance with sodium carbonate, to precipitate heavy metals. In some cases the metal is not precipitated completely in this way, *e.g.* Hg in presence of cyanides, Sb in tartar emetic, Fe, etc., in presence of tartrates or citrates. In such cases the liquid must be saturated with H_2S, in addition to the treatment with sodium carbonate, and then

To another portion add $BaCl_2$	The precipitate is insoluble in HCl, and is white	H_2SO_4, HF.
	The precipitate is soluble in HCl, and is white	H_3PO_4, $H_2S_2O_3$, H_3BO_3, H_3AsO_3, H_3AsO_4, H_2SiO_3, H_2SO_3, H_2CO_3.
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filtered. The filtrate is then rendered neutral by adding HNO_3 in slight excess, boiling to expel CO_2 and H_2S, making slightly alkaline with AmOH, and finally boiling till quite neutral.

216. Calcium Chloride Group.

To a portion of the neutral solution add acetic acid, and cool well. A precipitate of potassium hydrogen tartrate may be produced, if K_2CO_3 was employed instead of Na_2CO_3. Filter. To the filtrate add $CaCl_2$ solution in excess.

An immediate white precipitate of calcium oxalate indicates **Oxalic acid.** Confirm by placing the precipitate in dilute sulphuric acid, warming to 70°, and adding a solution of $KMnO_4$ drop by drop. This is decolourised by Oxalic acid.	To the filtrate add AmOH in slight excess, cool, shake well and allow to stand for 15 minutes. A white crystalline precipitate of calcium tartrate separates. Confirm by warming a portion of precipitate with H_2SO_4 and a small quantity of pyrogallol. Violet colouration indicates **Tartaric acid.** Confirm also by the reduction of ammoniacal silver solution.	To the filtrate add more calcium chloride if the other acids have been found, and boil to a small bulk: a white precipitate gradually forming indicates **Citric acid.** Confirm by warming the precipitate with strong H_2SO_4. Citric acid is slowly charred.

Formic and Acetic Acids.

217. To another portion of the neutral solution add a little ferric chloride solution. Formic and acetic acids both give a brown colouration in the cold, and on boiling, a brown precipitate of basic iron salt.

Confirm formic acid by

(*a*) The preliminary test with strong H_2SO_4.
(*b*) The reduction of $HgCl_2$.
(*c*) The reduction of $AgNO_3$.

Confirm acetic acid by

(*a*) The preliminary test with H_2SO_4.
(*b*) The formation of ethyl acetate.

DETECTION OF COMPLEX CYANOGEN ACIDS.

218. Such compounds as Prussian blue are insoluble in dilute mineral acids, and must be decomposed by caustic alkalies in order to detect the basic radicals which they contain, as well as the acids themselves. They are best examined as follows:

Boil a portion of the substance with sodium hydrate, and filter. The precipitate contains hydroxides of the heavy metals present, and may be examined for the metals in the usual way. The filtrate contains the soluble sodium salts of hydroferro- and hydroferricyanic acids and of thiocyanic acid. Acidify the filtrate with HCl, and add excess of $FeCl_3$. A precipitate of Prussian blue indicates hydroferrocyanic acid. Filter. A deep-red colour, or even a red tinge, in the filtrate indicates thiocyanic acid. To test for hydroferricyanic acid, which is rapidly reduced in presence of alkali to hydroferrocyanic, allow the first few drops of the filtrate to fall into an acidified solution of $FeSO_4$. A deep-blue precipitate of Turnbull's blue indicates the presence of hydroferricyanic acid. Confirm these by the reactions with $AgNO_3$.

PART II.

INTRODUCTION.

219. In Qualitative Analysis the chemical nature of the constituents of a mixture or of a compound is investigated, by converting those constituents into well-known and easily recognisable forms.

In Quantitative Analysis the same principles are involved, and the methods by which the quantitative determination of an element is carried out, are based upon the same reactions which serve for its qualitative recognition. The reactions selected, however, for quantitative work, must admit of the measurement of the amount of the constituent to be determined, either by converting it into a product which is of known composition, and can be weighed, or by measuring the volume of a prepared solution required to bring about the selected reaction.

The first is the **gravimetric** method, in which the substance to be determined is converted into another, of known composition, which is then accurately weighed. From this weight, the amount of the required constituent can be calculated.

The second is the **volumetric** method, in which solutions are employed, one containing the substance to be estimated, the other a known amount of a substance which has a definite reaction with the substance under examination. The volume of this second solution is measured, care being taken that the end of the reaction is sharply observed. This is usually attained by means of an **indicator,** such as litmus or methyl orange in acidimetry and alkalimetry.

Volumetric methods in general can be rapidly carried out, and require only simple apparatus. In many cases they admit

also of great accuracy. On the other hand, gravimetric methods are often tedious and cumbersome, and at times require elaborate apparatus. For rapidity of work, a volumetric method is to be preferred when one is available.

In all kinds of quantitative work, the most scrupulous care must be exercised to avoid possible errors; and if any slight error is even suspected, the experiment should be discarded and a new one commenced.

THE MEASUREMENT OF MASS.

220. The Balance. One of the operations most frequently carried out by the analyst is that of weighing. All quantitative experiments, whether gravimetric or volumetric, depend in the first instance upon this operation, which is therefore of very

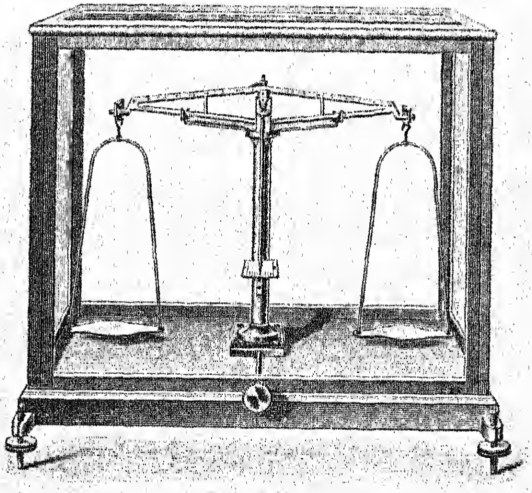

Fig. 45.

great importance. It can be carried out with great precision, this depending on the form of balance used, in the manner about to be described.

Only the special features of the chemical balance, a general view of which is shown in Fig. 45, will be considered here. To eliminate friction as far as possible, the turning centres at the middle and ends of the beam consist of knife-edges of agate, bearing on plates of the same material. A method of suspension of the pan is shown in Fig. 46. When the balance is out of use, the knife-edges are not in contact with the plates, the beam being supported upon arms from the central pillar. By turning the lever in front of the balance, these supports are caused, by means of a small crank or cam, to be withdrawn from the beam, which then rests on its knife-edges and is thus placed in action. The beam must always be supported while

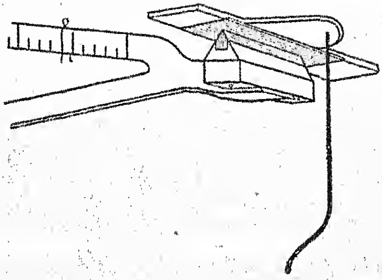

Fig. 46.

the weights or other articles on the pans are being changed. The movement of the beam is indicated by a pointer which descends from the middle of the beam to the scale near the foot of the pillar. When the weights on the two pans are equal, the pointer should swing to equal distances on both sides of the zero, or the swing should diminish by the same amount each time. A weighing is made by placing weights (Fig. 47) on the pan to measure to one centigram. Beyond this, the value of the remainder in milligrams and tenth-milligrams is determined by placing the rider, made of gold or platinum wire and weighing one centigram, upon the beam, and moving it until an exact adjustment is reached. The position of the rider on the graduated beam thus completes the measurement of weight to one-tenth of a milligram. For still more accurate weighing,

milligram weights are used on the pan, and a milligram rider to complete the weighing to the hundredth part of a milligram.

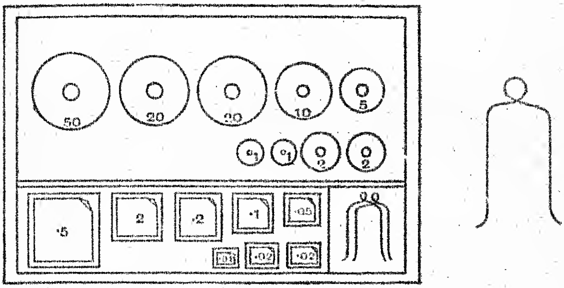

Fig. 47.

For all ordinary work, however, the centigram rider is quite sufficient.

221. The sensibility of the balance, that is, the degree to which the beam is displaced by a very small difference between the weights in the two pans, depends on several conditions. These may be briefly explained from the diagram (Fig. 48).

Let ACB represent the beam, the knife-edges being at those three points. Draw the horizontal line aCb, and the vertical

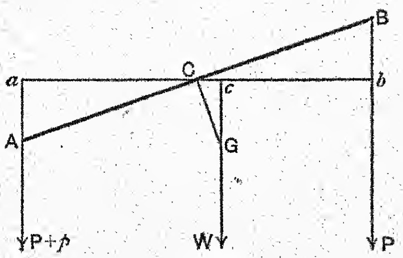

Fig. 48.

lines aA, cG, Bb. G is the centre of gravity of the beam, including the pans and their loads. Let W be the total weight of beam, pans, etc., P and $P+p$ the loads on the pans suspended

from B and A respectively. And let the angle aCA, through which the beam is displaced by the small difference p in the loads, when equilibrium is reached, be called θ.

Then since the sum of the moments about C is zero, we have

$$(P+p)\times aC = P\times bC + W\times cC\ ;$$

$$\text{but } aC = bC$$

$$\therefore\ p\times aC = W\times cC.$$

$$\text{Now the } \angle cGC = \angle aCA = \theta\ ;$$

$$\therefore\ aC = AC\cos\theta \text{ and } cC = CG\sin\theta\ ;$$

$$\therefore\ \frac{p}{W} = \frac{CG\sin\theta}{AC\cos\theta}\ ;$$

$$\therefore\ \tan\theta = \frac{p}{W}\frac{AC}{CG}.$$

Hence $\tan\theta$, and therefore also the angle θ through which the beam is turned, is increased by increasing p, the excess load in one pan, by increasing the length of the beam, by diminishing W, the weight of the beam, and by diminishing the distance of the centre of gravity from the knife-edge. The latter also increases the time of swing of the beam.

In practice these conditions are mutually antagonistic, and a compromise has to be effected. To ensure lightness, the beam is usually made with the central portion removed, which can be done without much loss of rigidity. The beam is also frequently made of aluminium or magnalium (an alloy of aluminium and magnesium), each having a low density. To lessen the time of swing of the beam, and therefore the time occupied in a weighing, the beam is shortened. This of course diminishes the sensibility, but the latter disadvantage is counterbalanced by making the depth of the centre of gravity below the knife-edge as small as is compatible with the stability of the balance.

This depth, and therefore also the sensibility of the balance, can be adjusted at will by raising or lowering a nut which turns, above the beam, on the central vertical axis.

The balance is enclosed in a glass case, the front of which, and usually also the back and sides, can be opened. The case must be kept closed to exclude dust, fumes, etc., and should contain a small glass dish of calcium chloride to keep the atmo-

sphere dry. The case is supported on three metal feet, which can be raised or lowered with screws, so that the balance may be levelled. The table on which balances are supported should be as rigid as possible, preferably one built into an external wall.

Many details of the construction of the balance, which have not been described, will readily be understood by examining the one in use.

222. Weighing bottles. When a substance is ready for analysis, it is placed at once in the weighing bottle. Some forms of this are shown in Fig. 49. The bottle should be of

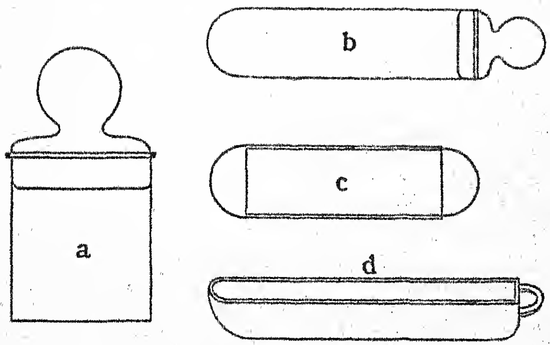

Fig. 49.

one diameter throughout, as *a*, *b*, and the ground glass stopper should not be cut, but blown from a glass tube, the flattened under side being retained. The two plain tubes shown at *c*, one fitting into the other, make a convenient form of weighing vessel for dried filters, etc. For insertion into a glass tube, a **boat** (Fig. 49, *d*) is often employed, as in the reduction of copper oxide (**71**), or the ignition of antimony sulphide (**311**). These boats are made of porcelain, glass, or platinum.

In addition to these, watch-glasses, porcelain dishes and crucibles, etc., may be used for weighing a substance. On no account should the substance to be weighed be placed directly on the pan.

Before weighing, a vessel must always be allowed to acquire, as nearly as possible, the temperature of the balance-room. With this object it is allowed to stand in the desiccator (**20**), in which also the weighing bottles should be kept.

THE MEASUREMENT OF VOLUME.

223. Flasks. In volumetric analysis, vessels are required which have an accurately known volume. These are of various kinds. For adjusting the volume of a solution, the measuring flask (Fig. 50) is best. This is a flask with a long, narrow neck, fitted with a ground-in glass stopper. The flask contains the definite volume marked on the side, when filled to the mark etched round the neck. It is important to remember that these flasks *contain* the quantity indicated, and that when the liquid is poured out, a little always remains adhering to the sides of the vessel. The volume is ascertained by weighing with water at a known temperature, which is indicated on the flask. It is only correct at this temperature.

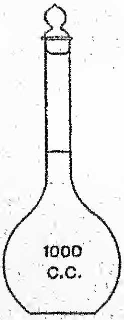

Fig. 50.

For an approximate measurement of the volume of a liquid, the measuring cylinder (Fig. 51) may be used.

224. Burettes. A burette is a graduated glass tube, from which liquids may be run by means of a tap at the bottom, and the quantity run off is thus measured. The tap may be of glass, or made by a short piece of rubber tube closed by a clip, and terminating in a glass jet, as shown in Fig. 52, which represents the usual forms of Mohr's burette. For some liquids, as solution of potassium permanganate, the rubber tube should not be used. The burette is held in a stand, so that the volume of the liquid may not be affected by touching the tube with the hands. The diameter of the tube should be uniform, and as the graduations are often made by linear measurement, any lack of uniformity in

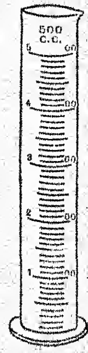

Fig. 51.

this respect will introduce an error. Such error can be detected and corrected by calibration (**226**).

To read the burette it is important that the eye of the observer should be on the *same level* as the surface of the liquid, the position of which is to be read. Since the surface of the liquid is concave, it is essential to read always the position of the same portion of the surface. The bottom of the meniscus is the most clearly defined position, and as this is several millimetres behind the graduated wall of the burette, it is obvious that any change in the level of the eye will cause also a change in the reading. Many devices are employed to obviate this difficulty. The *float* is one of these (Fig. 52), and consists of a closed tube, fitting easily into the burette, with a circular mark etched on it, and loaded with a little mercury, so that it just floats in the liquid with the top projecting above the surface. The position of the etched circle on the float is then easily seen on the graduated tube.

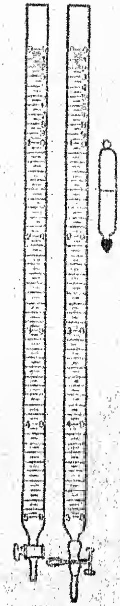
Fig. 52.

The burette is usually graduated in tenths of a cubic centimetre. When liquid is run from the burette, the sides of the tube remain wet with the liquid, and this slowly drains down. It will be found that on standing, the level of the liquid slowly rises by a small amount, and it is therefore necessary always to work at the same speed, and to read the burette just after the titration is finished.

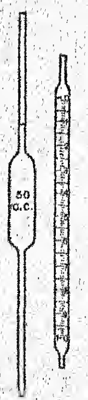

Fig. 53.

225. Pipettes. The pipette is employed for removing measured quantities of liquids from other vessels, and consists of a long tube, with or without a bulb at the middle, and having a circular mark etched on the upper straight portion. The lower end is contracted to a narrow opening. This form of pipette, and also the straight graduated form, is shown in Fig. 53. The pipette *delivers* the volume of liquid it is graduated for, and when this has run from it, a little

still remains in the lower end of the stem. As soon as the running has ceased, the end of the tube should be brought in contact with the liquid which has left it, and thus a little more is removed from the tube. The few drops which still remain are left in the tube, as they are taken into account in marking the pipette. By working always in the same manner, great uniformity in results can be attained.

The pipette is graduated at the temperature marked upon it, and may not be accurate at other temperatures. The correctness or error of the pipette should always be determined by calibration.

226. Calibration of apparatus. By this term is meant the measurement of the error, if any, in the graduation of volumetric apparatus. One possible cause of such error in the case of the burette has already been mentioned. The method of calibration generally adopted is to fill the instrument to the mark with distilled water at a known temperature, or with mercury, and find the weight of this water or mercury. From the known density of water at the working temperature (see appendix, **348**) the exact volume can be calculated.

Measuring flasks are weighed empty, then filled with the water and weighed again. The pipette is calibrated by running the water into a weighing bottle, emptying the pipette in the manner which is to be adhered to afterwards (**225**), and then weighing the water. In the case of the burette, the water is run out into the weighing bottle 5 c.cs. or 10 c.cs. at a time, and each quantity carefully weighed. The error at each 5 or 10 c.cs. can then be calculated, and it may be assumed to vary proportionally at the intermediate points. A curve may be drawn to obtain the errors at these points.

SECTION I.

VOLUMETRIC ANALYSIS.

EQUIVALENTS.

227. In comparing the reacting masses of chemical substances, it is necessary to fix upon a standard unit. The unit mass of hydrogen is chosen as this standard, because in all reactions involving this element, its mass is less than that of any of the other substances concerned.

In the case of elementary substances, the equivalent is defined as that quantity which combines with, or replaces, one gram of hydrogen. Most of the non-metallic elements combine directly with hydrogen, so that the equivalent is readily determined. With metals, no definite compounds are obtained, and the method of replacement of hydrogen, by solution of the metal in acids or in alkalies, may be applied in many cases.

The same considerations are extended to compounds, such as acids, alkalies, oxidising agents, the unit for determination of equivalents being always one part by weight of hydrogen.

When direct comparison of the substance with hydrogen is not possible, its equivalent may be determined by reference to a third element of known equivalent, *e.g.* chlorine, oxygen. Thus the equivalents of metals are accurately determined by analyses of the chlorides or oxides.

Again, the proportions may be determined in which metals replace each other from solutions of their salts, as, *e.g.* copper is precipitated by zinc from a solution of copper sulphate, and the relative equivalents are thus found.

Examples of some of these methods are given below.

DETERMINATION OF EQUIVALENTS.

A. By Replacement of Hydrogen.

228. The apparatus shown in Fig. 54 may be used. Weigh accurately about 0·5 gram of zinc, and dissolve in dilute sulphuric acid, measuring the volume of hydrogen liberated. Correct this volume for temperature and pressure, and obtain the volume of dry gas at 0° C. and 760 mm. Since one gram of hydrogen under those conditions occupies 11,160 c.cs., the equivalent of the metal is

$$\frac{\text{Weight of metal} \times 11{,}160}{\text{Corrected volume of hydrogen}}.$$

This method affords a means of estimating the amount of a metal whose equivalent is known, in a mixture with other materials which do not liberate a gas when heated with dilute acid, *e.g.* zinc dust.

Valuation of Zinc Dust.[1]

229. Weigh the zinc dust accurately into a 100 c.c. round flask, fitted with tap-funnel and two delivery tubes (Fig. 54). Cover the powder with water, and pass a stream of carbon dioxide through the flask to expel all air, collecting the gas in a measuring tube filled with caustic potash solution. When all the air is expelled, introduce from the tap-funnel a mixture of equal volumes of strong HCl and water, with a few drops of platinic chloride, and warm gently till the metal is dissolved. Expel the hydrogen remaining in the flask with carbon dioxide, and from the volume of gas obtained calculate the percentage of zinc in the sample.

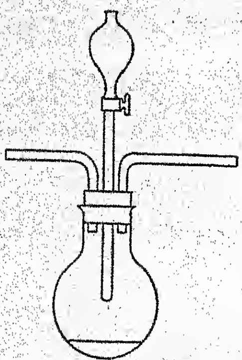

Fig. 54.

Another method, depending on the reducing power of zinc, will be given later (see par. 262).

[1] Gattermann, *Practical Methods of Organic Chemistry.*

B. By Reduction of Metallic Oxides.

230. Many oxides of metals are easily reduced to the metal, by heating either with carbon or hydrogen. For the determination of the equivalent it is best to carry out the reduction of an accurately known weight of the pure oxide with pure and dry hydrogen. In this way copper, nickel, cobalt, etc., are readily obtained from the oxides. Examples of the procedure are given in Part I., par. **71**.

C. By Synthesis of an Oxide from the Metal.

231. This method may be used to determine equivalents, when an oxide of definite composition is obtained.

For example, by igniting a weighed quantity of magnesium in a covered porcelain crucible, magnesium oxide, MgO, is obtained, and from this the equivalent of the metal may be deduced.

Again, by oxidising with nitric acid, most metals are converted into nitrates, if the temperature is kept low, these being decomposed on ignition into oxides. Thus copper, nickel, give first the nitrates, which on heating strongly leave a residue of the oxides, CuO, NiO. Tin is converted quantitatively into the dioxide, SnO_2.

D. By Replacement of one Metal by another.

232. Weigh accurately about 0·2 gram of pure zinc foil, and place it in a 200 c.c. conical flask. Add a solution of 2 grams silver nitrate in about 50 c.cs. distilled water, and allow to stand at the room-temperature, with frequent shaking, until all the zinc has been replaced by silver. *Warm gently, filter through a* tared filter, and wash thoroughly on the filter. Dry and weigh the residue of metallic silver.

Assuming the equivalent of silver to be 107·88, calculate that of zinc.

E. By Solution of the Metal in Standard Acid or Alkali.

This method will be described later in the section on alkalimetry (see par. **245**).

ACIDIMETRY AND ALKALIMETRY.

233. In volumetric analysis solutions of known strength are used, and, knowing the reactions of the substances in these solutions with other substances, the quantities of the latter in a given mixture or compound can be determined. For example, knowing that when sulphuric acid neutralises sodium carbonate the reaction is represented by the equation,

$$\underset{98}{H_2SO_4} + \underset{106}{Na_2CO_3} = Na_2SO_4 + H_2O + CO_2$$

it is easily seen (from the molecular weights of the reacting substances) that 98 parts by weight of sulphuric acid neutralise 106 parts of sodium carbonate. Therefore, given a solution of sulphuric acid containing, say, ·05 grs. per c.c., it is evident that each c.c. will neutralise $\cdot 05 \times \frac{106}{98}$ grs. of sodium carbonate.

Any solution of known strength is a **standard** solution, but much calculation may be saved if a certain definite strength is employed, and for this reason we use **normal** (N), **semi-normal** $\left(\frac{N}{2}\right)$, **decinormal** $\left(\frac{N}{10}\right)$, etc., solutions.

A normal solution of hydrochloric acid contains the molecular weight in grams of hydrochloric acid dissolved in a litre of the solution. Normal solutions of all acids are equivalent (*i.e.* 1 c.c. of N. HCl will neutralise as much of an alkali as 1 c.c. of N. H_2SO_4), and therefore must contain the same amount of replaceable hydrogen per litre, namely, 1 gr.

Thus from the formulae and basicities of the acids we get:

	Mol. Wgt.
N. Hydrochloric acid, - - - - - -	36·5
Monobasic, contains 36·5 grs. HCl per litre.	
N. Sulphuric acid, - - - - - - -	98
Dibasic, contains 49 grs. H_2SO_4 per litre.	
N. Nitric acid, - - - - - - - -	63
Monobasic, contains 63 grs. HNO_3 per litre.	

A normal solution of an alkali is equivalent to, or equi-volumetric with, a normal solution of an acid, *i.e.* 1 c.c. of the latter will neutralise 1 c.c. of the former, therefore

N. Sodium carbonate solution contains 53 grs. Na_2CO_3 per litre.
N. Sodium hydrate „ 40 grs. NaOH „
N. Potassium hydrate „ „ 56 grs. KOH „

When hydrochloric acid is added to silver nitrate, silver chloride is precipitated, and a solution of silver nitrate, of which 1 c.c. is precipitated by 1 c.c. of N. hydrochloric acid, is also normal; therefore

N. Silver nitrate ($AgNO_3$, Mol. Wt. 170) contains 170 grs. $AgNO_3$ per litre; similarly

N. Sodium chloride contains 58·5 grs. NaCl per litre.

A general definition may thus be given. A normal solution contains the equivalent weight in grams of the principal reacting element or radical dissolved in one litre of the solution. A slight modification of this definition must be made when solutions of oxidising agents are considered, but this will be explained later.

To prepare standard solutions, it is necessary to (*a*) weigh out and dissolve substances of known purity, or (*b*) roughly weigh or measure quantities of substances whose degree of purity is not known and find the correct strength of the solution thus made by titrating against a solution of known strength, *i.e.* one prepared by the former method.

PREPARATION OF STANDARD ACIDS.

234. The strengths of the concentrated acids are not known exactly, so we must proceed by the latter method in making standard solutions of these.

They may be titrated against a standard solution (a normal solution will save calculation) of sodium carbonate prepared as follows:

N. Sodium Carbonate.

235. Heat in a weighed platinum dish about 42 grs. of pure anhydrous sodium bicarbonate, with continual stirring, and without fusing; cool in the desiccator and weigh. Repeat the heating till the weight is constant.

Take out some of the pure sodium carbonate till exactly

26·5 grs. are left. Remove from the balance, add hot water, and heat till dissolved. Cool, transfer to a 500 c.c. flask and make up to the mark. Mix well before using. The solution contains ·053 grs. of sodium carbonate per c.c. and is therefore normal.

PREPARATION AND STANDARDISATION OF SULPHURIC ACID.

236. Measure 28 c.cs. of strong sulphuric acid in a measuring cylinder, and pour into water. When cold, transfer to a litre flask and make up to one litre at the room temperature (about 15° C.). The solution will be roughly normal, since the strong acid contains, approximately, 98 per cent. H_2SO_4.

Rinse out a burette with water, then two or three times with a few c.cs. of the acid, and fill the burette with acid. Do not attempt to get the acid exactly at the zero.

Rinse a 25 c.c. pipette with water, then two or three times with a little of the N. sodium carbonate solution, and finally fill the pipette.

Run the alkali into a 250 c.c. conical flask, and then touch the surface of the liquid with the end of the pipette. Do not blow out the liquid left in the end of the pipette.

Add to the alkali one or two drops of litmus solution, read the position of the acid in the burette, enter the reading immediately in the note-book, and run the acid carefully into the flask till the litmus just turns red. Boil to drive off the carbon dioxide liberated by the acid. The litmus becomes blue again. Add more acid till the solution is turned red with one drop after boiling. Read the burette. NOTE.—Before the end of every titration the liquid on the sides of the flask should be washed down.

Methyl orange may be used as an indicator in place of litmus, as it has the advantage of not being affected by carbonic acid, and therefore the solution does not require to be boiled.

Repeat the titration, using litmus or methyl orange, till three concordant results are obtained. Average these, and calculate the strength of the acid as follows :

Write first the equation, and find the weights of the reacting substances.

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2.$$

then 1 c.c. of N. Na_2CO_3 solution contains ·053 grs. Na_2CO_3;
∴ 1 " " " " will neutralise ·049 grs. of H_2SO_4.

Now suppose 24·2 c.cs. of acid have been required for 25 c.cs. of the N. sodium carbonate. These must contain

$$25 \times \cdot 049 \text{ grs. of } H_2SO_4.$$

∴ 1 c.c. of the sulphuric acid contains

$$\frac{25 \times \cdot 049}{24 \cdot 2} = \cdot 0506 \text{ grs. } H_2SO_4.$$

Another method of calculation is the following:

25 c.cs. of N. Na_2CO_3 solution neutralise 24·2 c.cs. of H_2SO_4;

$$\therefore \text{ the } H_2SO_4 \text{ solution is } \frac{25}{24 \cdot 2} \text{ of normal;}$$

$$\therefore \text{ 1 c.c. of the acid contains } \frac{25}{24 \cdot 2} \times 0 \cdot 049 = \cdot 0506 \text{ grs. } H_2SO_4.$$

237. N. Sulphuric acid. To make the sulphuric acid normal, 25 − 24·2 or ·8 c.cs. of water must be added to each 24·2 c.cs. of the sulphuric acid. Measure the acid left, in a measuring cylinder, add the calculated quantity of water and again titrate. The solutions should be equivolumetric, *i.e.* the sulphuric acid is normal. If not, again add a calculated quantity of water.

238. N. Sodium hydrate. The sodium hydrate powder (98 per cent.) may be used. Roughly weigh out enough to make a litre of solution slightly stronger than normal, say 45 grs. Dissolve in water, and when cold, make up to a litre.

Take 25 c.cs. in a pipette, place in a titrating flask, add one drop of methyl orange solution and run in the sulphuric acid (now normal) as before. Assume 25·3 c.cs. of acid are required.

Then the alkali is $\frac{25 \cdot 3}{25}$ normal, *i.e.* 1 c.c. contains

$$\frac{25 \cdot 3}{25} \times \cdot 040 = \cdot 041 \text{ grs. of NaOH.}$$

If the solution is required to be normal, add ·3 c.c. of water for each 25 c.cs. of alkali.

In the following estimations the standard solutions will not be taken as normal. This will give the student good practice in calculation.

Estimation of KOH in Caustic Potash (sticks).

239. Given sulphuric acid, 1 c.c. = ·0253 grs. H_2SO_4.

Weigh a dry corked tube containing about 10 grs. of the stick potash. Transfer the stick to water in a 250 c.c. flask and reweigh the tube and cork. Allow the caustic potash to dissolve, and when cold make up to 250 c.cs. Use 25 c.cs. for each titration, with methyl orange or litmus as indicator.

The results should be entered as under.

Tube and caustic potash,	22·84 grs.
Tube, - - - -	12·95 „
Caustic potash, - -	9·89 „

Titrations:	1.	2.	3.	
	24·98	26·88	24·52	
	·52	2·39	1·10	
	24·46	24·49	24·42	Average 24·46 c.cs.

$$\underset{112}{2KOH} + \underset{98}{H_2SO_4} = K_2SO_4 + 2H_2O.$$

1 c.c. of acid contains ·0253 grs. of H_2SO_4;

∴ 1 c.c. of acid will neutralise $\cdot0253 \times \frac{112}{98}$ grs. KOH,

and 24·46 c.cs. „ „ „ $\frac{\cdot0253 \times 112 \times 24\cdot46}{98}$ grs. KOH,

but 24·46 c.cs. „ „ „ 25 c.cs. of the caustic potash solution;

∴ 25 c.cs. of the solution contains $\frac{\cdot0253 \times 112 \times 24\cdot46}{98}$ grs. of KOH;

∴ 250 c.cs. of the caustic potash solution or 9·89 grs. of the sticks contain $\frac{\cdot0253 \times 112 \times 24\cdot46 \times 10}{98}$ grs. of KOH;

∴ per cent. of KOH in the sticks is $\frac{\cdot0253 \times 112 \times 24\cdot46 \times 10 \times 100}{98 \times 9\cdot89}$

$= \underline{73\cdot19}.$

Estimation of Na_2CO_3 in Soda Crystals.

Given 1 c.c. of sulphuric acid contains ·0253 grs. H_2SO_4.

240. Powder the crystals, and if moist, dry between layers of filter paper. Weigh out about 10 grs. from a stoppered bottle, dissolve in water and make up to 250 c.cs. Titrate 50 c.cs. at a time, using methyl orange as indicator.

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2.$$

1 c.c. of acid contains ·0253 grs. H_2SO_4;

$\therefore$ 1 c.c. of acid will neutralise $\cdot 0253 \times \frac{106}{98}$ grs. of Na_2CO_3,

$= \cdot 0274$ grs. of Na_2CO_3.

It will be an advantage, when doing many estimations of the same substance, to calculate the strength of the standard solution in terms of the substance to be found, as above, before proceeding with the calculation.

Enter results as before.

Bottle and crystals,	30·61	grs.
Bottle, - - -	20·16	"
Crystals, -	10·45	"

Titrations with 50 c.cs.	1.	2.	3.	
	30·16	30·04	29·86	
	2·18	2·04	1·90	
	27·98	28·00	27·96	Average 27·98 c.cs.

27·98 c.cs. of acid $= 27\cdot98 \times \cdot0274$ grs. Na_2CO_3;

$\therefore$ 250 c.cs. of solution or 10·45 grs. crystals contain

$27\cdot98 \times \cdot0274 \times 5$ grs. Na_2CO_3;

$\therefore$ per cent. of Na_2CO_3 in crystals $= \frac{27\cdot98 \times \cdot0274 \times 5}{10\cdot45} \times 100.$

$= \underline{36\cdot68}.$

Estimation of HCl in Concentrated Hydrochloric Acid.

241. Given sodium hydrate solution equivalent to the sulphuric acid used in the previous experiments, *i.e.* 1 c.c. $= \cdot0253$ grs. H_2SO_4;

$\therefore$ 1 c.c. $= \cdot0253 \times \frac{36\cdot5}{49}$ grs. HCl $= \cdot0188$ grs. HCl.

Pour 7 or 8 c.cs. of concentrated hydrochloric acid into a weighed stoppered bottle. Weigh the bottle and acid. Wash the contents into a 250 c.c. flask and make up to the mark. Take 50 c.cs. for each titration and run in caustic soda solution, using methyl orange as indicator. Take the mean of three concordant titrations, and calculate the result as in the preceding examples.

Estimation of CH_3COOH in Acetic Acid.

242. Given 1 c.c. sodium hydrate solution $= \cdot 0253$ grs. H_2SO_4. Acetic acid is a monobasic acid, mol. wt. 60;

$\therefore$ 60 grs. acetic acid $=49$ grs. sulphuric acid;

$\therefore$ 1 c.c. sodium hydrate solution $= \cdot 0253 \times \frac{60}{49}$ grs. CH_3COOH.

Place about 4 c.cs. of acetic acid in a weighed stoppered bottle, and proceed as for hydrochloric acid.

NOTE. Methyl orange cannot be used for organic acids, and is replaced by phenolphthalein (1 gr. solid in 100 c.cs. of alcohol). Its neutral solution is colourless, and alkaline solution pink. The colour of phenolphthalein is destroyed by carbon dioxide.

Estimation of Sodium Hydrate and Sodium Carbonate in Soda Ash.

243. Given 1 c.c. sulphuric acid $= \cdot 048$ grs. H_2SO_4;

$\therefore$ 1 c.c. „ „ $= \cdot 0519$ grs. Na_2CO_3,

and 1 c.c. „ „ $= \cdot 0392$ grs. $NaOH$.

Weigh out about 10 grs. of soda ash, dissolve in water and make up to 500 c.cs. Take 50 c.cs. for each titration. Add a few drops of phenolphthalein and slowly run in the acid from the burette until the red colour of the liquid is just destroyed. Read the burette. At this stage the whole of the sodium hydrate will have been neutralised and the sodium carbonate will have been converted to bicarbonate.

$$2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4.$$

Now add a little methyl orange and run in acid till the yellow colour changes to pink.

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

It will be seen that the sulphuric acid required for the latter operation is equal to that used in the previous one for the conversion of the carbonate to bicarbonate. Hence, by doubling this volume of acid, we have that required for the complete neutralisation of the carbonate, and by subtracting the volume so obtained from the total acid used, we have the volume required to neutralise the sodium hydrate.

Example.

	Weight of soda ash used, - - - -	10 grs.
	Volume of acid for first operation, - -	10·0 c.cs.
	Total volume of acid used, - - - -	18·9 ,,
	Volume used in second operation, - -	8·9 ,,
∴	Volume used for neutralisation of carbonate,	17·8 ,,
and	,, ,, ,, ,, hydrate, -	1·1 ,,

∴ Weight of NaOH in 50 c.cs. solution or 1 gr. of sample

$$= 1{\cdot}1 \times {\cdot}0392 = {\cdot}0431\ ;$$

∴ Percentage of NaOH = $\underline{4{\cdot}31}$.

and weight of Na_2CO_3 in 50 c.cs. solution or 1 gr. of sample

$$= 17{\cdot}8 \times {\cdot}0519 = {\cdot}9248\ ;$$

∴ Percentage of $Na_2CO_3 = \underline{92{\cdot}48}$.

NOTE. The student should repeat this experiment, using pure sodium carbonate to test the accuracy of the method.

In technical work the alkali present is generally given as so much Na_2O. Although this substance does not exist as such in the solutions, equations may be written assuming its presence, and the calculation made as before ; thus,

$$\underset{98}{H_2SO_4} + \underset{62}{Na_2O} = Na_2SO_4 + H_2O,$$

therefore if 1 c.c. sulphuric acid = ·048 grs. H_2SO_4,

1 c.c. ,, ,, $= {\cdot}048 \times \frac{62}{98} = {\cdot}0304$ grs. Na_2O.

In the last estimation the total Na_2O will be

$$18{\cdot}9 \times {\cdot}0304 \times 10 = \underline{57{\cdot}45} \text{ per cent.}$$

As further exercises, the strengths of nitric acid, sulphuric acid, ammonium hydrate solutions, oxalic acid, tartaric acid, etc., may be estimated.

Estimation of NH_4 in Ferrous Ammonium Sulphate.

Given acid and alkali (equal) 1 c.c. = ·0253 gr. H_2SO_4.

244. Fit up the apparatus shown in the sketch (Fig. 55). Crush and dry the salt. Weigh into the flask *A*, an amount sufficient to produce enough ammonia to neutralise about 20 c.cs. of the acid. Place in the flask *C*, 25 c.cs. of the standard acid. Add a small excess of alkali to the salt and keep boiling for about 20 minutes. The arrangement of the flasks *B* and *C* prevents the acid from rushing back into *A*. Keep the flasks *B* and *C* cool with water. Wash the contents into one flask and titrate the excess of acid with standard alkali. Subtract the volume required from 25 c.cs. to obtain the volume of acid neutralised by the ammonia.

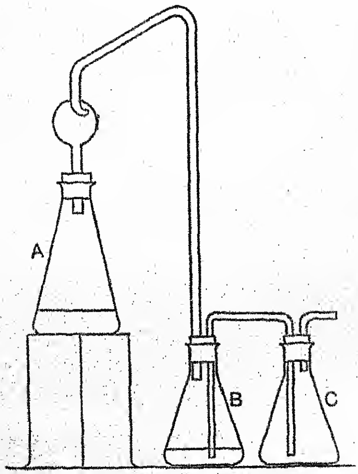

Fig. 55.

To calculate the result,

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4;$$

$$\therefore \ H_2SO_4 \text{ corresponds to } 2NH_4,$$

or 98 parts by weight correspond to 36 parts NH_4.

$$1 \text{ c.c. of acid} = \cdot 0253 \text{ grs. } H_2SO_4.$$

$$1 \ \text{,,} \ \text{,,} = \cdot 0253 \times \tfrac{36}{98} \text{ grs. } NH_4.$$

To determine the Equivalent of Magnesium by use of Standard Acid.

Given N. sulphuric acid and N. sodium hydrate.

245. The acid contains 1 gr. of replaceable hydrogen per litre. Weigh accurately about ·4 gr. of magnesium into a titrating

flask, add a little water, and then slowly add 50 c.cs. of the sulphuric acid. The metal dissolves completely in the acid. Titrate the excess of acid with alkali and thus find the volume of acid neutralised by the magnesium. Assume this to be 33 c.cs.

Calculate as follows.

1 c.c. of acid = ·001 gr. hydrogen ;

∴ 33 c.cs. " " = ·033 gr. "

·033 grs. of hydrogen are replaced by ·4 gr. magnesium.

$$\therefore\ 1\ \text{''}\quad \text{''}\quad \text{is}\quad \text{''}\quad \text{''}\ \frac{\cdot 4}{\cdot 033} = \underline{12{\cdot}1.}$$

Or the weight of metal required to neutralise 1 litre of the N. sulphuric acid may be calculated. This is the equivalent. In the same way find the equivalent of zinc, and of aluminium. The latter will require a stronger solution of acid, say five times normal.

To determine the Equivalent of Zinc, using the Oxide.

Given acid and alkali as before.

246. Use as before 50 c.cs. of the acid. Weigh out and dissolve in the acid 1·5 grs. of zinc oxide. Titrate the excess of acid with sodium hydrate.

Calculate as follows. Assume the acid used = 37 c.cs.

37 c.cs., *i.e.* ·037 grs. of hydrogen = 1·5 grs. zinc oxide ;

$$1\ \text{gr.}\ \text{''}\quad \text{''}\quad = \frac{1{\cdot}5}{\cdot 037} = 40{\cdot}5\ \text{grs. of zinc oxide.}$$

This 40·5 must consist of the equivalent of oxygen (the oxygen combining with 1 part of hydrogen) united to that of the zinc, and therefore the equivalent of zinc, will be found by subtracting 8. ∴ equivalent of zinc = 40·5 − 8 = <u>32·5</u>.

Repeat with other oxides, as MgO.

STANDARD SOLUTIONS OF OXIDISING AGENTS.

Potassium Permanganate.

$KMnO_4$.

247. Potassium permanganate in presence of a reducing agent will give up a portion of its oxygen. Sulphuric acid is

always added to prevent the precipitation of the manganese as oxide. In such cases the potassium and manganese are left as potassium and manganous sulphates, and therefore the amount of available oxygen is shown by the following equation:

$$\underset{2\times 158.}{2KMnO_4} + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + \underset{5\times 16.}{5O}.$$

Thus we see that 316 parts by weight of potassium permanganate supply 80 parts by weight of oxygen available for oxidation.

A normal solution of an oxidising agent is one which contains, in one litre, the equivalent weight in grams of oxygen available for oxidation.

Therefore a normal solution of potassium permanganate contains 31·6 parts of the salt per litre.

The principal reacting element here is oxygen, but though the 31·6 grs. of the salt contain 12·8 grs. of oxygen, only 8 grs. are available for oxidation.

Action of Potassium Permanganate on Ferrous Salts.

248. In oxidations by potassium permanganate, we need only consider the available oxygen, thus:

$$\underset{10\times 56.}{10FeSO_4} + 5H_2SO_4 + \underset{5\times 16.}{5O} = 5Fe_2(SO_4)_3 + 5H_2O.$$

From this, we see that 10 atoms of iron (atomic weight 56) are oxidised by 5 atoms of oxygen, or 560 parts by weight of iron by 10 equivalents of oxygen.

We may now write:

1 litre of $\frac{N}{10}$ potassium permanganate contains 3·16 grs. $KMnO_4$.

1	"	"	"	"	yields	·8 grs. O.
1	"	"	"	"	oxidises	5·6 grs. Fe.

$\frac{N}{10}$ Potassium Permanganate.

249. Weigh out exactly 3·16 grs. of the purest potassium permanganate, dissolve in water, and make up to one litre.

See that all the salt is dissolved before using.

Estimation of Fe in Ferrous Ammonium Sulphate.

$FeSO_4.(NH_4)_2SO_4.6H_2O$.

250. Weigh out about 4 grs. of the salt, dissolve in water, adding a few drops of sulphuric acid, and make up to 250 c.cs. Take 50 c.cs. for each titration and add dilute sulphuric acid. Run in the permanganate. As the permanganate is reduced its colour is destroyed, and therefore when the oxidation is complete, one drop will colour the liquid permanently.

1 c.c. $\frac{N}{10}$ potassium permanganate contains ·00316 grs. $KMnO_4$;

∴ ,, ,, ,, ,, will oxidise ·0056 grs. Fe.

Enter results, and calculate as in previous estimations.

Estimation of Fe in Iron Wire.

Given 1 c.c. of potassium permanganate = ·00316 grs. $KMnO_4$
= ·0056 grs. Fe.

251. Fit up two small flasks with stoppers and tubes, so that a current of carbon dioxide may be sent through them (Fig. 56). Place the flasks on an iron or asbestos plate, standing on a tripod, and in each, place 60-70 c.cs. of dilute sulphuric acid. Boil the acid to expel air, and then pass the carbon dioxide through the flasks. Place in each flask about 0·1 gram of iron wire, accurately weighed, and continue the current of gas until all the iron has dissolved. Titrate the whole of the solution in each flask at one operation, and without loss of time. If the results do not agree, repeat the experiment.

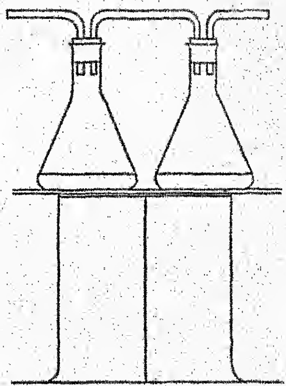

Fig. 56.

Estimation of Fe in Iron Alum.

$K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$.

Given 1 c.c. of potassium permanganate = ·0056 grs. Fe.

252. The iron in this salt is in the ferric state, and must be reduced to the ferrous condition for titration with permanganate.

Weigh accurately into a small flask about ·6 grs. of iron alum, dissolve in water, and add sulphuric acid. Place in the liquid a few pieces of zinc (free from iron) and allow the action to continue until all the zinc is dissolved. To see whether the reduction is complete, take out a drop on the end of a fine glass rod and touch with it, a drop of a solution of potassium thiocyanate on a white plate. If a red colour is produced, more zinc, and possibly acid, must be introduced. If the reduction is found complete, titrate the whole as soon as the zinc has dissolved.

The student should try the action of other reducing agents, as sulphuretted hydrogen or sulphur dioxide, taking care that none of the reducing agent is left when titrating.

Estimation of Fe in Haematite.

(Fe_2O_3.)

Given $\frac{N}{10}$ permanganate solution.

253. Grind the haematite very finely in an agate mortar. Weigh accurately about ·7 gr. and dissolve in strong hydrochloric acid on a water-bath. Reduce the iron to the ferrous state by adding stannous chloride in slight excess. Remove the excess of stannous chloride by adding excess of mercuric chloride solution. Dilute to 250 c.cs. and titrate 50 c.cs. at a time.

Estimation of Oxalic Acid, $(COOH)_2$, in Commercial Oxalic Acid.

254. When oxalic acid is oxidised, water and carbon dioxide are produced.

$$\underset{90}{(COOH)_2} + \underset{16}{O} = H_2O + 2CO_2.$$

Thus 8 parts of oxygen oxidise 45 parts of anhydrous oxalic acid.

$$1 \text{ c.c. } \frac{N}{10} \text{ potassium permanganate} = \cdot 0008 \text{ grs. oxygen};$$

$$\therefore 1 \text{ ,, ,, ,, ,,} = \cdot 0045 \text{ grs. } (COOH)_2.$$

Weigh out 1·5 grs. of oxalic acid, dissolve in water, and make up to 250 c.cs. Take 25 c.cs. for each titration, add dilute sulphuric acid and run in a few c.cs. of the permanganate. The action is very slow in the cold, but takes place readily at 60° C. Heat the flask and continue adding the permanganate till the oxidation is complete. Calculate the percentage of oxalic acid.

Estimation of Oxalic Acid in Oxalates.

255. Oxalic acid is liberated from oxalates by the addition of sulphuric acid, therefore proceed as in the last estimation.

Estimation of Ca in Calcium Carbonate.

Given $\frac{N}{10}$ potassium permanganate.

256. Weigh about ·7 grs. of Iceland spar into a beaker, add water and dilute hydrochloric acid, and cover with a clock-glass. When dissolved, dilute to about 100 c.cs., heat nearly to boiling, add a slight excess of ammonium hydrate, and then a moderate excess of ammonium oxalate. Allow the liquid to settle, filter and wash well with hot water. Make a hole at the bottom of the filter paper and wash as much as possible of the precipitate through into a 250 c.c. flask. Wash the filter paper with warm dilute hydrochloric acid to remove all the oxalate. Add a few c.cs. of strong sulphuric acid to the liquid, make up to 250 c.cs. and titrate 50 c.cs. at a time.

$$1 \text{ c.c. } \frac{N}{10} \text{ potassium permanganate} = \cdot 0045 \text{ grs. } (COOH)_2;$$

$$\therefore 1 \text{ ,, ,, ,, ,,} = \cdot 0020 \text{ grs. Ca.}$$

Estimation of $NaNO_2$ in Sodium Nitrite.

Given $\frac{N}{10}$ potassium permanganate.

257. Nitrites are decomposed by dilute acids, nitrous acid being liberated. The nitrous acid is extremely unstable, and even in dilute solutions splits up, liberating nitric oxide:

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The production of nitric oxide (red gas with air) would mean loss of nitrous acid. The estimation should be carried out as follows:

Weigh out about 2 grs. of sodium nitrite, dissolve in water, and make up to 500 c.cs. Take 25 c.cs. for each titration. With the first 25 c.cs. run in about 10 c.cs. of the permanganate, add a few drops of dilute sulphuric acid, and shake. The colour of the permanganate disappears. Now run in more permanganate (with addition of sulphuric acid if necessary) till a permanent colour is produced. The reduction near the end of the action is slow, and the solution must be allowed to stand. When finished read the burette.

Take another 25 c.cs. and run in nearly the volume of permanganate used in the first titration. Add a little acid, and then run in permanganate till the oxidation is complete. The smell of the contents of the flask will indicate whether there is loss of nitric oxide. Repeat the experiment and obtain three results which agree.

$$\underset{69}{NaNO_2} + \underset{16}{O} = NaNO_3.$$

1 c.c. $\frac{N}{10}$ potassium permanganate $= \cdot 0008$ grs. O ;

$\therefore$ 1 „ „ „ „ $= \cdot 00345$ grs. $NaNO_2$;

or 1 „ „ „ „ $= \cdot 00235$ grs. HNO_2.

STANDARD POTASSIUM DICHROMATE SOLUTION.

258. Like potassium permanganate, this solution is an oxidising agent, and from each molecule of the salt, three atoms of oxygen are available for oxidation:

$$\underset{294}{K_2Cr_2O_7} + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + \underset{48}{3O}.$$

Hence 294 grs. of potassium dichromate yield 48 grs. of oxygen available for oxidation, and therefore a normal solution will contain 49 grs. of the salt per litre. A decinormal solution (4·9 grs. per litre) is generally used.

Preparation of $\frac{N}{10}$ Dichromate Solution.

259. Gently fuse a little over 5 grs. of pure potassium dichromate in a porcelain dish and then powder in a dry mortar.

Weigh out exactly 4·9 grs., dissolve in water and make up to a litre.

1 c.c. $\frac{N}{10}$ potassium dichromate contains ·0049 grs. $K_2Cr_2O_7$;

∴ 1 „ „ „ „ yields ·0008 grs. O;

∴ 1 „ „ „ „ oxidises ·0056 grs. Fe.

Estimation of Fe in Ferrous Ammonium Sulphate.

260. Carry out the experiment as with potassium permanganate, except in the indication of the end point. With potassium dichromate the reduced solution, which contains chromium sulphate, is green in colour, and it is impossible to distinguish the colour produced by one drop of potassium dichromate in this liquid. The use of an external indicator is resorted to, and the mode of use is as follows:

In a test-tube place a small crystal of potassium ferricyanide, and wash it several times with water; then add water to make a very dilute solution. By means of a glass rod place a series of drops of this solution on a white tile or plate, and from time to time during the titration with the dichromate, take out from the flask, on the end of a glass rod, a little of the solution and touch with it one of the drops. If much ferrous iron is present, a strong blue colour will be produced. This will become fainter as more dichromate is added, and finally the drop will give only a faint brown colour. The oxidation is then complete. Calculate as with potassium permanganate.

Estimation of Fe in Spathic Iron Ore.

261. Grind the ore very finely. Weigh out ·5 gr. and dissolve in the apparatus used for the estimation of iron in iron wire, using a mixture of equal volumes of strong hydrochloric acid and water. Dilute with air-free water to 5 times the volume, and titrate the whole at once with potassium dichromate.

By this process the ferrous iron alone is estimated.

To estimate the *total* iron, take a similar weight of ore, dissolve as before, but there is no necessity to take precautions against oxidation. Do not use much hydrochloric acid in either

process or chlorine will be liberated by action with the dichromate.

When dissolved, add 10-15 c.cs. of strong sulphuric acid; add some zinc, and reduce as with haematite (**253**). Titrate the whole at once. Calculate the ferrous iron as FeO, and the ferric as Fe_2O_3.

Valuation of Zinc Dust.

262. This material is largely used as a reducing agent, its value for this purpose depending on the amount of metallic zinc present. It usually contains, however, a large proportion of zinc oxide, together with other impurities.

A method for its valuation is based on the reduction of potassium dichromate. Make a $\frac{1}{2}$-N. solution of dichromate by dissolving 4·9 grs. and making up to 200 c.cs. This solution should oxidise 3·25 grs. (one-tenth equivalent) of zinc. Weigh out accurately about 0·5 gr. of the zinc dust, place it in a 250 c.c. flask, and add 50 c.cs. of the dichromate solution. Now add dilute sulphuric acid, little by little, with gentle shaking, until the zinc is completely dissolved, and then make up to the mark with water. The dichromate solution would now have been of decinormal strength, but it has been partly reduced. Prepare 100 c.cs. of $\frac{N}{10}$ ferrous ammonium sulphate solution, and titrate 10 c.cs. of this with the reduced dichromate, repeating the titration until several concordant results are obtained. Suppose that 18·5 c.cs. of dichromate are required, and that the weight of zinc dust used is 0·57 gr.

Then, since only 10 c.cs. of decinormal dichromate would have been required, the dichromate is $\frac{10}{18 \cdot 5}$ of decinormal. Therefore 250 c.cs. contain

$$\frac{250 \times 0 \cdot 0049 \times 10}{18 \cdot 5} \text{ grs. } K_2Cr_2O_7,$$

and the amount of dichromate reduced by the zinc is

$$\frac{250 \times 0 \cdot 0049 (18 \cdot 5 - 10)}{18 \cdot 5} \text{ grs.}$$

The weight of zinc equivalent to this is

$$\frac{250 \times 0{\cdot}00325(18{\cdot}5 - 10)}{18{\cdot}5} \text{ grs.,}$$

and therefore the amount of zinc in the sample of zinc dust is

$$\frac{250 \times 0{\cdot}00325(18{\cdot}5 - 10) \times 100}{18{\cdot}5 \times 0{\cdot}57}$$

$$= 65{\cdot}5 \text{ per cent.}$$

STANDARD SILVER NITRATE SOLUTION.

263. The molecular weight of silver nitrate is 170, and as each molecule contains one atom of silver and silver is monovalent, a normal solution of the salt will contain a gram molecule in a litre, *i.e.* the equivalent weight in grams of silver per litre.

A decinormal solution is generally used.

Preparation of $\frac{N}{10}$ Silver Nitrate Solution.

Dissolve exactly 4·25 grs. of silver nitrate in distilled water and make up to 250 c.cs.

Estimation of Cl in Sodium Chloride.

$$\underbrace{\underset{108+14+48}{AgNO_3}}_{170} + \underbrace{\underset{23+35{\cdot}5}{NaCl}}_{58{\cdot}5} = AgCl + NaNO_3.$$

1 c.c. $\frac{N}{10}$ silver nitrate contains ·0170 grs. $AgNO_3$;

∴ 1 c.c. $\frac{N}{10}$ " " " ·0108 grs. Ag.

and 1 c.c. $\frac{N}{10}$ " " precipitates ·00355 grs. Cl.

264. Weigh about 1 gr. of pure sodium chloride, dissolve in distilled water and make up to 250 c.cs. Take 50 c.cs. for each titration. Add one or two drops of potassium chromate (K_2CrO_4) solution as indicator and run in the silver nitrate. The silver nitrate first precipitates silver chloride, and only when the whole of this is precipitated will the red silver chromate be produced. Therefore when one drop gives a permanent

red colouration the chloride is all precipitated. Calculate the percentage of chlorine.

Given the equivalent of chlorine as 35·45, calculate the equivalent of sodium.

$\frac{N}{10}$ Sodium Chloride.

265. The student should calculate the amount of pure salt necessary for this preparation and make up the solution. It should then be titrated against the $\frac{N}{10}$ silver nitrate as a check on the working. Such a solution may be used to estimate silver volumetrically.

Estimation of Cl in Tap-water.

266. Make a centinormal solution of silver nitrate, by diluting 25 c.cs. of the decinormal solution to 250 c.cs. Take 50 c.cs. of the tap-water for each titration.

Calculate the result in grains per gallon.

1 gallon = 70,000 grains.

70 c.cs. water = 70 grs. or 70,000 m.grs.

Therefore the actual weight, in m.grs., of chlorine in 70 c.cs. of tap-water, will give the number of grains per gallon.

Bromides and iodides may be estimated in a similar way to chlorides.

Standard Solutions of Iodine and Thiosulphate.

267. The usefulness of iodine in volumetric analysis depends largely upon its reaction with sodium thiosulphate, the iodine combining with part of the sodium. The action is represented by the following equation :

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

By this action we are enabled to estimate iodine present in any solution in the free state.

Iodine gives with starch paste an intensely blue coloured substance commonly known as iodide of starch. If a solution of sodium thiosulphate is added to starch so coloured, the iodine reacts with the sodium thiosulphate as mentioned above and

the blue colour is destroyed. The solutions of iodine and thiosulphate generally used are decinormal and are prepared as below.

$\frac{N}{10}$ Iodine.

268. If we regard the free iodine in solution, the equivalent of iodine being 127, we must dissolve 12·7 grs. per litre for a decinormal solution. If we consider the iodine solution as an oxidising agent acting according to the equation,

$$I_2 + H_2O = 2HI + O,$$

we again arrive at the amount 12·7 grs. to yield 0·8 grs. of oxygen, *i.e.* a decinormal solution.

Weigh out exactly 12·7 grs. of powdered purest resublimed iodine into a litre flask. Add about 20 grs. of pure potassium iodide and 200 c.cs. of water and shake until the iodine is dissolved. Then make up to a litre. Keep well stoppered and in the dark.

$\frac{N}{10}$ Sodium Thiosulphate.

269. The sodium thiosulphate solution will be equivolumetric with the iodine, and we must therefore weigh out a gram molecule of the salt (see equation) for a normal solution, and one-tenth of this for a decinormal solution, and make up to a litre.

The same value is arrived at if we take the principal reacting element, *i.e.* the sodium which unites with the iodine.

Weigh out 24·8 grs. of the pure salt, $Na_2S_2O_3 . 5H_2O$, into a litre flask, dissolve in water and make up to one litre. Keep well stoppered and in the dark.

Equalisation of the Solutions.

Take 25 c.cs. of the iodine solution and run in thiosulphate from the burette. The colour of the iodine solution becomes fainter as the iodine enters into combination with the sodium, and when only a very faint yellow colour remains, add starch paste. This immediately produces a deep-blue colour. Now add the thiosulphate drop by drop, shaking well after each

addition, till the blue colour just disappears. Read the burette. If the solutions have been accurately made with pure substances they will be found equivolumetric. If not, equalise by adding water to the stronger and find the strength of the sodium thiosulphate (and therefore also the iodine) as follows.

Standardisation of Sodium Thiosulphate by means of Dichromate.

270. Measure 25 c.cs. of $\frac{N}{10}$ potassium dichromate into a titrating flask, add about 2 grs. of solid potassium iodide, and then 5 c.cs. pure HCl. The hydrochloric acid is oxidised by the dichromate, and the chlorine so obtained liberates its equivalent of iodine. The liquid becomes dark-brown in colour, and contains the equivalent of 25 c.cs. of $\frac{N}{10}$ iodine solution. Titrate as before with the thiosulphate, adding starch paste when the free iodine is nearly all removed. The colour of the liquid is now composed of the brown of free iodine, the blue of starch iodide, and the green of the chromium chloride. Continue the addition of thiosulphate carefully until first the yellow colour, and then the blue, is discharged, leaving a pure green solution. With a little practice, the end point can be accurately determined.

If the thiosulphate solution is exactly decinormal, 25 c.cs. should be required to unite with the iodine liberated by 25 c.cs. of dichromate. From the volume actually used, the strength of the thiosulphate may be calculated.

Estimation of Chlorine in Chlorine Water.

271. Dissolve 7-8 grs. potassium iodide in a little water contained in a 250 c.c. flask. Add 50 c.cs. chlorine water, and make up to the mark. Titrate the liberated iodine, using 25 c.cs. for each titration.

Estimation of Bromine in Bromine Water.

272. Add 50 c.cs. of bromine water to a 250 c.c. flask containing a solution of 10 grs. of potassium iodide. Make up to the mark and titrate as with chlorine water.

Estimation of MnO_2 in Commercial Manganese Dioxide.

273. Grind to very fine powder and weigh about ·5 gr. into a small flask with ground-in delivery tube (Fig. 57). Add 25 c.cs. of strong hydrochloric acid and some small pieces of magnesite, and connect to the U-tubes, the first of which contains 4 grams and the second 2 grs. of potassium iodide

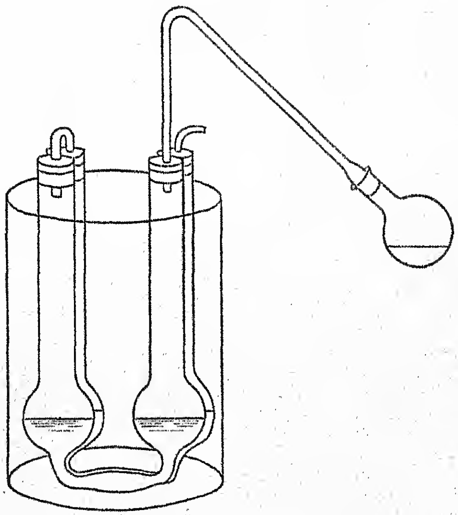

Fig. 57.

dissolved in water. The bulbs should be less than half filled. Heat gently. The chlorine evolved liberates iodine, which remains in solution. At the end of the action, gently boil the liquid in the small flask to drive off the chlorine. The magnesite, which dissolves slowly in hydrochloric acid, is placed in the flask at the beginning of the experiment, in order to provide a stream of carbon dioxide at the close. This prevents the liquid sucking back, and drives out the chlorine completely.

When the distillation is finished, wash the contents of the U-tubes into a 250 c.c. flask, make up to the mark, and take 50 c.cs. for each titration.

$$\underset{87}{MnO_2} + 4HCl = MnCl_2 + 2H_2O + \underset{2\times 35.5.}{Cl_2}.$$

1 c.c. of thiosulphate $= \cdot 0127$ grs. I
$= \cdot 00355$ grs. Cl
$= \cdot 00435$ grs. MnO_2.

Estimation of available Chlorine in Bleaching Powder.

274. Weigh about 10 grs. of bleaching powder into a mortar, add a little water, and grind to a thin cream. Pour the milky liquid into a litre flask and grind the residue with a little more water, and repeat till all the substance is in the flask. Make up to a litre. Shake well, take out 25 c.cs., add 10 c.cs. of a solution of 5 grs. potassium iodide in 100 c.cs. of water, and acidify with acetic acid. The liberated chlorine displaces an equivalent quantity of iodine. Titrate with thiosulphate and calculate the amount of chlorine as in previous estimations.

$$Ca{<}^{Cl}_{OCl} + 2KI + 2CH_3COOH = I_2 + 2KCl + Ca(C_2H_3O_2)_2 + H_2O.$$

Estimation of Hypochlorite.

Use the solution prepared as directed in par. **38.**

275. Make up the whole solution to 500 c.cs. Of this take 10 c.cs. and place it in a 250 c.c. flask. Add a solution of 7-8 grams potassium iodide in water, acidify the whole with acetic acid, make up to the mark and mix well. Titrate 50 c.cs. at a time with the thiosulphate. From the result calculate the amount of hypochlorite in the original solution.

$$NaOCl + 2KI + 2CH_3COOH = I_2 + NaCl + 2CH_3COOK + H_2O.$$

Estimation of Arsenious Acid.

276. This is oxidised to arsenic acid by means of free iodine;

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI.$$

Weigh out 2 grams of sodium arsenite, dissolve in water and make up to 250 c.cs. Measure 25 c.cs. of this solution into a

titrating flask, add an equal bulk of a saturated solution of sodium bicarbonate to neutralise the hydriodic acid which will be formed, and some starch solution, and titrate with iodine until a permanent blue colour is just obtained.

A similar experiment may be made with sodium arsenate. Weigh out 2 grams, dissolve in water, add some acetic acid and boil for a few minutes to decompose any nitrite in the material. Cool and make up to 250 c.cs. Estimate any arsenious acid in the sample by titrating 25 c.cs. as above.

To determine the arsenic acid, take 100 c.cs. of the solution, reduce by saturating with sulphur dioxide and then boiling off the excess, and make up the cold solution to 200 c.cs. Titrate 50 c.cs. of this liquid, after adding $NaHCO_3$ and starch, with the iodine solution. This gives the total amount of arsenic, and hence the amount of arsenic acid in the original sample may be calculated.

Estimation of Antimony.

277. Antimony trioxide may also be oxidised and estimated by means of standard iodine:

$$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI.$$

As in the estimation of arsenic, the hydriodic acid set free must be neutralised with sodium bicarbonate.

Weigh out about 2 grams of tartar emetic,

$$K(SbO)C_4H_4O_6 \cdot \tfrac{1}{2}H_2O,$$

dissolve in water, and make up to 250 c.cs. Titrate 25 c.cs. at a time, adding an equal bulk of saturated solution of sodium bicarbonate and a little starch solution, with standard iodine.

Estimation of Sulphurous Acid in Aqueous Solution.

278. Measure 5 c.cs. of freshly prepared sulphurous acid into a 250 c.c. flask containing 100 c.cs. of standard iodine solution. The latter must be in excess, so that the colour is not entirely discharged. Make up to the mark, and titrate the excess of iodine, 50 c.cs. at each titration, with thiosulphate.

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$

The estimation may also be made, but less accurately, by

diluting 10 c.cs. of the sulphurous acid solution to 500 c.cs., and running this from a burette into 25 c.cs. of the standard iodine.

Estimation of Sulphurous Acid in a Soluble Sulphite.

279. Weigh about one gram of sodium sulphite into a 250 c.c. flask, dissolve in water, acidify with acetic acid and run in a slight excess of iodine solution. Make up to the mark and titrate the excess of iodine with thiosulphate.

Estimation of Hydrogen Sulphide in Aqueous Solution.

280. Prepare a dilute solution of sulphuretted hydrogen in water, and titrate 50 c.cs. with iodine in presence of starch until the blue colour appears. The reaction

$$H_2S + I_2 = 2HI + S$$

is not quantitative if more than 0·04 per cent. of hydrogen sulphide is present. If more than this quantity is found, therefore, dilute the solution to a sufficient degree and repeat the experiment.

Preparation of Standard Soap Solution.

281. Place in a litre flask about 10 grs. of sodium oleate or Castile soap, add 500 c.cs. of methylated spirit and allow the soap to dissolve. Make up to a litre with distilled water and shake well. To standardise the solution, prepare the following solution of a calcium salt.

Weigh out exactly 1 gr. of Iceland spar into a porcelain dish, and add a little dilute hydrochloric acid, covering the vessel with a clock glass. Allow the substance to dissolve, and then evaporate to dryness on a water bath. Redissolve the residue in distilled water and again evaporate, to complete the removal of the hydrochloric acid. Now dissolve the residue in distilled water and make up to one litre. Each c.c. of this solution contains calcium chloride equivalent to ·001 gr. of calcium carbonate.

Take 20 c.cs. of this solution in a stoppered bottle of 250 c.cs. capacity and add 50 c.cs. of distilled water.

Run in the soap solution from a burette, 1 c.c. at a time, and shake the bottle vigorously after each addition. When a slight lather is obtained add the soap more carefully till a permanent lather is obtained. This lather should last at least two minutes. Read the burette and calculate the volume of water to be added to the soap solution in order that 21 c.cs. shall produce a lather with 20 c.cs. of the calcium solution. The additional 1 c.c. of soap solution is required to produce a lather with 70 c.cs. of distilled water.

The soap solution is now of such strength that 1 c.c. will precipitate ·001 gr. of calcium carbonate or its equivalent.

Since 0·001 gr. in 70 c.cs. (70 grs.) is 1 part in 70,000, the number of milligrams in 70 c.cs. is equal to the number of grains per gallon.

With this solution, always use 70 c.cs. of the water to be tested, subtract 1 c.c. from the volume of soap solution used, and the remainder will give the number of grains of calcium carbonate present in, or equivalent to the magnesium and other salts present in, one gallon.

Estimation of the Hardness of Water.

Total Hardness.

282. Take 70 c.cs. of water in the stoppered bottle, and titrate with the soap solution. Subtract 1 c.c. from the volume of soap solution used, and the remainder gives the number of grains per gallon. Repeat the experiment.

Permanent Hardness.

Take about 170 c.cs. of the water in a flask and counterpoise on a rough balance. Boil the water for half an hour to remove the temporary hardness. Cool and make the liquid up to its original weight with distilled water, filter through a dry filter paper, take 70 c.cs. of the filtrate and titrate as before.

Subtract the permanent hardness from the total hardness, to obtain the temporary hardness.

SECTION II.

GRAVIMETRIC ANALYSIS.

TO DETERMINE THE WEIGHT OF A FILTER ASH.

283. Before weighing a precipitate in a gravimetric estimation, it should be more or less strongly heated, in order that moisture may be completely expelled, unless the high temperature causes decomposition. Some precipitates are merely dried

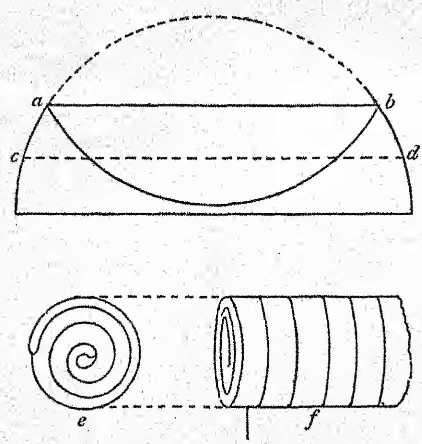

Fig. 58.

at 100° and then weighed, the filter itself having previously been weighed. In case of ignition, the filter, which retains some of

the precipitate, is burned, and the ash added to the precipitate. The weight of this ash, which is known, is then deducted from the total weight.

To determine the weight of the ash of the filters used, weigh a porcelain or platinum crucible. Fold a filter along a diameter (Fig. 58), and twice more along the lines *ab* and *ad* respectively. Then roll this strip tightly into a narrow roll, as at *e*, and bind it in a spiral manner with a long platinum wire, like *f*. Now burn this by touching it with the flame of the burner, holding the burning coil over the crucible, which stands meanwhile on a sheet of glazed paper. When the flame and the red glow which succeeds it are both extinct, there still remains much unburnt carbon. Again touch this with the flame repeatedly, but do not keep the flame playing on it, until all the carbon is burnt, and the ash alone remains. Shake this into the crucible. Repeat until five or six filters have been burned, and then, with a camel-hair brush, transfer any fragments which have dropped on the paper into the crucible. Ignite strongly for fifteen minutes, allow to cool in the desiccator, and weigh. Calculate the weight of ash from one filter, and compare your result with the value marked on the packet.

ESTIMATION OF COPPER.

284. A. By Precipitation as Hydroxide and Conversion of this into Oxide by Ignition.

Weigh out accurately 0·8-1 gram of pure copper sulphate, $CuSO_4 . 5H_2O$, into a 500 c.c. beaker, and dissolve in about 100 c.cs. distilled water, adding a few drops of dilute HCl. Heat to boiling, and add NaOH solution as long as a precipitate forms. Cover the beaker with a clock-glass, and boil until the precipitate turns black. Allow to settle, test the clear liquid with litmus paper, and if alkaline, filter at once, pouring the clear liquid through the filter, and allowing the precipitate to remain in the beaker. To this add boiling water, boil for a few minutes, and again pour the clear liquid through the filter. Repeat this washing by decantation several times, and then transfer the precipitate to the filter, using the wash bottle and glass rod. If some of the precipitate adheres to the sides of

the beaker, detach it by rubbing with the glass rod, having a short piece (1 cm.) of tightly-fitting rubber tube on the end. Now continue to wash the precipitate on the filter, allowing each washing to run through completely before adding the next, until a few drops of the liquid from the funnel give no turbidity with $BaCl_2$ solution, even on standing for five minutes.

When the precipitate is completely washed, cover the funnel with filter paper, and dry in the steam oven. Transfer the precipitate as completely as possible to a weighed porcelain (or better, platinum) crucible, fold the paper, with the soiled part in the centre, into a tight roll, bind this with platinum wire, and burn the paper until no carbon is left. Allow the ash to drop into the crucible, first shaking the precipitate to one side. Moisten the ash with two drops of strong nitric acid to reoxidise reduced copper, dry gently over a small flame, and then ignite the whole strongly for 15-20 minutes. Allow to cool in the desiccator and weigh. Repeat the ignition until the weight is constant.

The method of calculating and entering the result will be given here as an example.

Weight of bottle and copper sulphate (*a*),	12·3312	grs.
" " " " (*b*),	11·4060	"
" copper sulphate used,	·9252	"
" crucible, copper oxide and ash (*a*),	14·1510	"
" " " " (*b*),	14·1510	"
" crucible,	13·8575	"
" copper oxide and ash,	·2935	"
" ash,	·0005	"
" copper oxide,	·2930	"

Now copper oxide is known to contain 63·57 parts of copper in 79·57 of oxide; therefore the amount of copper in 100 parts of the salt used is given by the expression

$$Cu = \frac{0{\cdot}2930 \times 63{\cdot}57 \times 100}{79{\cdot}57 \times 0{\cdot}9252} \text{ per cent.}$$

$$= 25{\cdot}30 \text{ per cent.}$$

Theoretically, $Cu = 25{\cdot}46$,,

Error $= -0{\cdot}16$,,

285. B. **By precipitation as cupric sulphide, and conversion of this into cuprous sulphide by ignition with sulphur.**

Weigh out and dissolve the copper sulphate as above, add a few drops of HCl (the solution should be free from nitric acid), heat nearly to boiling, and pass H_2S gas until the liquid is saturated and all the copper precipitated as black CuS. Allow to settle, and filter at once. Wash with warm H_2S water until a few drops, on adding HCl and $BaCl_2$, give no turbidity. Keep both filter funnel and beaker covered with clock-glasses during the filtration and washing, to avoid oxidation of the sulphide. Dry the precipitate quickly, transfer to a Rose crucible (Fig. 59), adding the filter ash also, cover the contents of the crucible with powdered sulphur, and ignite in a current of dry hydrogen until all free sulphur is expelled. Allow to cool at first in the current of hydrogen, and when nearly cold place in the desiccator. After weighing, repeat the ignition with sulphur until the weight is constant. The residue is cuprous sulphide, Cu_2S. From the weight of this calculate the amount of copper as above.

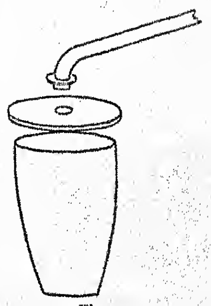

Fig. 59.

This method of estimating copper is chiefly employed in separations. *The metal may also be precipitated as sulphide by* adding $Na_2S_2O_3$ solution, or as cuprous thiocyanate, $Cu_2(SCN)_2$, by adding ammonium thiocyanate in presence of sulphurous acid, with subsequent conversion into Cu_2S by Rose's method. Copper cannot be precipitated completely as hydroxide in presence of non-volatile organic acids, sugars, etc.

ESTIMATION OF SULPHURIC ACID, (SO_4).

286. By precipitation as barium sulphate, $BaSO_4$. Use copper sulphate. Weigh out the salt as above, acidify the solution with hydrochloric acid, heat to boiling and add about 20 c.cs. of ammonium chloride solution, to render the subsequent precipitate of $BaSO_4$ more granular and therefore more easily

filtered. To the boiling liquid add slowly a boiling solution of $BaCl_2$ as long as a precipitate forms. Allow to settle, wash by decantation several times with hot water, and then on the filter until the water gives no turbidity with $AgNO_3$ solution. Dry, ignite in a platinum or porcelain crucible, and weigh. If much of the precipitate adhered to the filter, moisten the ash with a few drops of HCl, add two drops of H_2SO_4, to convert BaS into $BaSO_4$. Dry carefully, and ignite. Repeat the ignition till the weight is constant. From the weight of $BaSO_4$ calculate the SO_4.

ESTIMATION OF WATER OF CRYSTALLISATION.

287. A. In crystallised copper sulphate, $CuSO_4 . 5H_2O$.

Dry some of the finely powdered salt by pressing between several layers of filter paper, and then leaving it exposed to the air for a short time. Weigh two watch-glasses held with rims together in a wire clip. Place in the glass 1-1·5 grams of the salt and weigh again. Now heat in the air-bath to 120-130° for an hour, separating the glasses meanwhile. Allow to cool in the desiccator, and weigh with the glasses closed. Repeat the heating until the weight is constant. The loss represents $4H_2O$. To determine the remaining molecule of water, heat at 250-260° until a constant weight is obtained. Calculate the percentage in each case.

288. B. In crystallised zinc sulphate, $ZnSO_4 . 7H_2O$. This salt loses 6 molecules of water at 100°, the last molecule only at a low red heat. Proceed as above and determine the loss at 120-130°: for the last molecule use a porcelain crucible and heat with the burner to dull redness until the weight is constant.

289. C. In crystallised barium chloride, $BaCl_2 . 2H_2O$.

This salt loses all its water at 113°. Determine the loss at 120-130°.

A complete analysis of copper sulphate has now been affected. Tabulate the results thus :

	Found.	Calculated.
Copper (as CuO), - -		25·46
„ (as Cu_2S), - -		(25·46)
SO_4, - - - -		38·47
$4H_2O$, - - - -		28·86
$1H_2O$, - - - -		7·21
		100·00

ESTIMATION OF BARIUM.

290. By precipitation as barium sulphate. Use crystallised barium chloride. Weigh 0·7-0·8 grs. into a 500 c.c. beaker, add a little dilute HCl, heat to boiling and precipitate the $BaSO_4$ by gradual addition of a boiling solution of sulphuric acid or ammonium sulphate. Proceed exactly as in the estimation of SO_4 in copper sulphate. From the weight of $BaSO_4$ calculate the amount of Ba.

ESTIMATION OF CHLORINE.

291. By precipitation as silver chloride, AgCl. Weigh 0·5 grams of barium chloride, dissolve in water and acidify with nitric acid. Add a solution of silver nitrate until no more precipitate forms, and then either allow to stand overnight in the dark, or boil gently for fifteen minutes for immediate filtration. The liquid should be protected from strong light. Allow to settle, and filter, washing by decantation with hot water, and then on the filter until free from silver. Dry, and transfer the precipitate to a porcelain crucible, ignite over a small flame till the chloride begins to fuse, and weigh. Burn the filter, place the ash in the crucible and weigh again. This last increase, less the weight of the ash, gives the weight of silver reduced by the burning of the paper. Calculate the weight of chloride equivalent to this, and add to the weight of the precipitate. Or convert the reduced silver into chloride by placing the ash on the inverted crucible lid, adding two drops of strong nitric acid to dissolve the silver, and then hydrochloric to reprecipitate as chloride. Dry carefully and ignite until fused. From the weight of silver chloride calculate that of the chlorine.

This method is a very accurate one. Compare the volumetric estimation of chlorides, etc., by titration with standard silver nitrate (**264**).

A complete analysis of barium chloride has now been made. Tabulate the results :

	Found.	Calculated.
Barium, - - - -		56·23
Chlorine, - - - -		29·02
Water, - - - -		14·75
		100·00

ESTIMATION OF SILVER.

292. By precipitation as silver chloride. Weigh out 0·5 gram of silver nitrate, dissolve in water and acidify with nitric acid. Precipitate the silver with a slight excess of hydrochloric acid, and complete the estimation as described above for chlorine. From the weight of silver chloride calculate that of the silver present.

293. Estimation of bromine in a bromide. Estimation of Iodine in an Iodide. Weigh out 0·3-0·4 gram of potassium bromide or iodide, acidify with nitric acid, precipitate with a slight excess of silver nitrate, and treat the precipitated silver bromide or iodide as directed for silver chloride.

ESTIMATION OF ZINC.

294. A. **By precipitation as zinc carbonate, and conversion of this into oxide, ZnO, by ignition.** Weigh out about 1 gram of zinc sulphate, $ZnSO_4 . 7H_2O$, into a large porcelain dish, dissolve in about 100 c.cs. water, cover the dish with a clock-glass, heat to boiling, and slowly add solution of sodium carbonate in excess. Precipitation is not complete in presence of ammonium salts, and these, if present, must be expelled by boiling the liquid containing excess of sodium carbonate. Filter, wash several times by decantation, and then on the filter till free from sodium carbonate. To prevent reduction of ZnO in burning the filter, and consequent loss of zinc by volatilisation, the filter, after removing the precipitate as

completely as possible, may be moistened with a strong solution of ammonium nitrate and again dried, and then burned alone. Ignite the whole until the weight is constant, and from the weight of zinc oxide calculate that of the zinc.

295. B. **By precipitation as zinc sulphide in alkaline solution, and weighing the anhydrous ZnS.** Weigh about 1 gram of zinc sulphate into a 200 c.c. Erlenmeyer flask, dissolve in about 100 c.cs. of water, add AmOH in slight excess, heat nearly to boiling, and pass a rapid current of H_2S until the liquid is saturated. Nearly fill the flask with water saturated with H_2S, close it with a cork and allow to stand overnight. Filter, wash with water containing ammonium sulphide, and keep the funnel covered with a glass plate.

The dry precipitate is then transferred to a Rose crucible, the filter ash added, the whole covered with powdered sulphur and ignited in a stream of dry hydrogen. The ignition is repeated until the weight is constant.

ESTIMATION OF IRON.

296. **By precipitation as ferric hydroxide, $Fe(OH)_3$, and ignition of this to oxide, Fe_2O_3.** Weigh about 1·5 grams of ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 . 6H_2O$, dissolve in 100 c.cs. water, acidify with sulphuric acid, and add 2-3 c.cs. strong HNO_3. Cover the beaker with a clock-glass, and boil *gently for ten minutes to oxidise the iron to ferric salt.* When oxidation is complete (ascertain this by mixing a drop of the solution with a drop of freshly prepared ferricyanide solution on a porcelain dish, when there should be no blue colour), add AmOH solution in slight excess, heat nearly to boiling, and filter at once, washing by decantation and on the filter until $BaCl_2$ solution produces no turbidity. If ammonium chloride was present in the solution, it must also be completely removed from the precipitate by washing, testing finally with $AgNO_3$ solution.

Dry the precipitate, transfer to a platinum or porcelain crucible, add the filter ash, and ignite strongly for 20 minutes at a time, until the weight of Fe_2O_3 is constant. From this calculate the weight of Fe.

ESTIMATION OF ALUMINIUM.

297. **By precipitation as hydroxide, $Al(OH)_3$, and ignition of this to the oxide, Al_2O_3.** Weigh about 1·5 grams of potash alum, dissolve in 100 c.cs. water, add some ammonium chloride solution, and precipitate with a slight excess of AmOH. Boil until the excess of ammonia is nearly expelled, and then filter and wash. The precipitate must be strongly ignited, as it retains traces of water to a high temperature.

ESTIMATION OF CHROMIUM.

298. A. **By precipitation as hydroxide, $Cr(OH)_3$, and ignition of this to oxide, Cr_2O_3.** Weigh out about 1 gram of chrome alum, $Cr_2(SO_4)_3 . K_2SO_4 . 24H_2O$, or about 0·7 gram of potassium dichromate, $K_2Cr_2O_7$, and dissolve in 100 c.cs. water. In the latter case, reduce the dichromate completely to chromium salt with sulphurous acid, or by heating with 5 c.cs. alcohol and an equal bulk of strong HCl, until all alcohol and aldehyde are expelled. Precipitate with AmOH in slight excess, and heat until the excess of ammonia is nearly removed and the liquid is quite colourless. Complete the estimation as for iron or aluminium.

B. **By precipitation as lead chromate, $PbCrO_4$, which is weighed.** This method is described under lead (304).

ESTIMATION OF NICKEL.

299. **By precipitation as nickelous hydroxide, $Ni(OH)_2$, and conversion of this into oxide, NiO, by ignition.** Weigh about 1 gram of nickel ammonium sulphate, $Ni(NH_4)_2(SO_4)_2 . 6H_2O$, into a 500 c.c. beaker; dissolve in water, adding a few drops of HCl, precipitate with a slight excess of sodium hydrate or carbonate, and heat to boiling. Wash by decantation with boiling water several times, boiling at each washing, and then on the filter until $BaCl_2$ produces no turbidity. Dry, and ignite strongly in a platinum or porcelain crucible. The residue is NiO.

This residue may be easily reduced to metallic nickel by Rose's method of heating in a current of hydrogen (285). The reduced metal is allowed to cool at first in the current of hydrogen, and the ignition repeated until the weight of metal is constant.

ESTIMATION OF COBALT.

300. By precipitation as hydroxide, and reduction of this to metal, which is weighed. This is the most accurate method of determining cobalt. Weigh about 1 gram of cobalt potassium sulphate and dissolve in water, or 0·5 gram of cobalt oxide and dissolve in a little strong HCl, evaporating on the steam to expel the excess of acid. Dissolve the residue in water, and precipitate the cobalt with a slight excess of caustic soda or potash. Heat to boiling and boil until the precipitate is almost black. Filter, wash by decantation with boiling water, and then on the filter until free from sulphate or chloride as the case may be. Ignite the precipitate in a porcelain crucible with Rose cover, in a stream of dry hydrogen, until the weight is constant. The residue is metallic cobalt.

ESTIMATION OF CALCIUM.

301. By precipitation as calcium oxalate, CaC_2O_4, which is converted by ignition into carbonate or oxide. Weigh about 0·5 gr. of Iceland spar into a beaker, and dissolve in dilute HCl, covering the beaker with a clock-glass. Boil to expel carbon dioxide, add AmOH in excess, and to the hot solution add ammonium oxalate solution as long as a precipitate forms. Boil for twenty minutes, and then allow the precipitate to settle completely. Decant the clear liquid through a filter, and wash several times by decantation with hot water, and then on the filter until completely free from ammonium oxalate.

Dry the precipitate in the steam oven, place in a platinum or porcelain crucible, burn the filter and place the ash also in the crucible. The oxalate may be converted into carbonate by heating gently over a small flame, so that the bottom of the crucible is scarcely red. It is better, however, with the quantity used above, to convert directly into oxide, CaO, by heating for

twenty minutes over the blowpipe, or with a Mecker burner, until the weight is constant. From the weight of calcium oxide calculate that of the calcium.

ESTIMATION OF OXALIC ACID.

302. **By precipitation as calcium oxalate.** Weigh about 0·8 gr. of pure ammonium oxalate, $(NH_4)_2C_2O_4 . H_2O$, dissolve in water, add a little acetic acid and heat to boiling. Precipitate calcium oxalate by adding excess of a clear solution of calcium acetate, and treat the precipitate as described above. From the weight of calcium oxide calculate the equivalent amount of (C_2O_4) or of oxalic acid.

ESTIMATION OF LEAD.

303. A. **By precipitation as sulphate, $PbSO_4$, which is weighed.** Weigh about 1 gram of crystallised lead acetate, $Pb(C_2H_3O_2)_2 . 3H_2O$, dissolve in 50-60 c.cs. water, and add a little acetic acid. Keep the liquid cold, and add dilute sulphuric acid until no more precipitate forms. Add alcohol equal in bulk to the liquid, mix well, and allow to stand overnight. This ensures complete precipitation of the lead sulphate, which is slightly soluble in water alone. Filter, and wash with 50 per cent. alcohol until all H_2SO_4 is removed.

Place the dry precipitate in a porcelain crucible, burn the filter on the crucible lid, and moisten the ash with two drops HNO_3 and one drop dilute H_2SO_4, to reconvert any reduced lead or PbS into $PbSO_4$. Dry carefully, and ignite the whole to dull redness until the weight is constant.

304. B. **By precipitation as chromate, $PbCrO_4$, which is weighed.** Weigh about 0·8-1 gram of lead acetate or nitrate, dissolve in water, add a little acetic acid and some sodium acetate solution, and precipitate the lead with excess of potassium chromate. Allow the precipitate to settle, filter through a weighed filter, wash first by decantation with cold water and then on the filter. Dry at 100° until the weight is constant. The residue is $PbCrO_4$.

This method may also be employed for the estimation of chromium.

305. C. Lead may also be estimated as sulphide, PbS, by the method given for copper (in acid solution, **285**), or for zinc (in alkaline solution, **295**).

ESTIMATION OF STRONTIUM.

306. By precipitation as sulphate, $SrSO_4$, which is weighed. Weigh about 1 gram of strontium carbonate, $SrCO_3$, and dissolve in dilute HCl, covering the beaker with a clock-glass. Add 60-70 c.cs. distilled water, and precipitate the strontium as sulphate, as described above for lead (**303**). Strontium sulphate is also slightly soluble in water.

Dry the precipitate and ignite it as described for barium sulphate. The residue is $SrSO_4$.

ESTIMATION OF MAGNESIUM.

307. By precipitation as magnesium ammonium phosphate, $MgNH_4PO_4.6H_2O$, and conversion of this by ignition into magnesium pyrophosphate, $Mg_2P_2O_7$. Weigh out about 1 gram of magnesium sulphate, $MgSO_4 . 7H_2O$, dissolve in 50-60 c.cs. water, add some AmCl solution, and then AmOH in excess. If a precipitate forms, add more AmCl until it redissolves. Now add excess of sodium phosphate and stir well, taking care that the glass rod does not touch the beaker. Remove the rod, rinsing it into the beaker, cover the beaker with a clock-glass, and allow to stand over-night.

Filter, and wash with a mixture of 1 part AmOH (·880) and 3 parts water, the precipitate being slightly soluble in water. Continue washing on the filter until the filtrate gives no turbidity with $AgNO_3$, after acidifying with HNO_3. Dry the precipitate, transfer to a platinum or porcelain crucible, add the filter ash, and ignite, gently at first until water and ammonia are expelled, and then strongly until the weight is constant. The residue is magnesium pyrophosphate, $Mg_2P_2O_7$. From its weight calculate the weight of magnesium.

ESTIMATION OF PHOSPHORIC ACID.

308. Weigh out about 1 gram of sodium phosphate, $Na_2HPO_4 . 12H_2O$, dissolve in water, add some AmOH, and

excess of magnesia mixture (a solution of magnesium sulphate or chloride in presence of AmCl and AmOH), and treat the precipitate exactly as described above. From the weight of $Mg_2P_2O_7$ calculate that of the phosphoric acid.

ESTIMATION OF ARSENIC.

309. A. **The above method** may also be used for this purpose. The arsenic must be in the form of arsenate, as sodium arsenate, $Na_2HAsO_4 . 12H_2O$. Arsenious compounds may be oxidised by heating in solution with HCl and a little $KClO_3$. When completely oxidised, make alkaline with ammonia, and precipitate with magnesia mixture in the form of magnesium ammonium arsenate, $MgNH_4AsO_4 . 6H_2O$. Treat the precipitate exactly as the corresponding phosphate, except that it must be ignited, with the Rose crucible cover, in a current of dry oxygen. When the weight of magnesium pyrarsenate, $Mg_2As_2O_7$, is constant, the amount of arsenic, or of arsenic acid, may be calculated.

This method is used for the separation of arsenic from antimony, and also, with a slight modification, from tin.

310. B. **By precipitation as arsenic trisulphide, As_2S_3, which is weighed.** Weigh about 0·8 gram of sodium arsenite into a 300 c.c. Erlenmeyer flask, dissolve in water, acidify with HCl, and add a few grams of tartaric acid. Fit the flask with a doubly-bored stopper carrying two right-angled tubes, one passing to the bottom of the flask for the supply of sulphuretted hydrogen, and the other ending just beneath the cork, and dipping into water in a second flask. This arrangement protects the liquid in the first flask from air. The arsenic solution is heated nearly to boiling and is then saturated with sulphuretted hydrogen. After standing for some time until the precipitate has settled, the excess of sulphuretted hydrogen is removed from the liquid by passing a current of carbon dioxide gas, and the liquid is then filtered through a weighed filter. After washing with water containing sulphuretted hydrogen until the washings are free from chloride, the precipitate is dried at 100° and weighed.

If the precipitate contains sulphur, it must be converted into

arsenic acid by oxidation with strong HNO_3, and the arsenic then estimated as magnesium pyrarsenate as in method A.

A volumetric method for the estimation of arsenic is given in par. 276.

ESTIMATION OF ANTIMONY.

311. A. **By precipitation as antimony trisulphide, Sb_2S_3, which is weighed.** Weigh about 1 gram of tartar emetic, $K(SbO)C_4H_4O_6 . \frac{1}{2}H_2O$, and treat exactly as described for the precipitation of arsenic trisulphide, except that the solution should be kept gently boiling during the latter part of the precipitation with sulphuretted hydrogen. After removing the excess of gas with carbon dioxide, filter through a weighed filter, dry at 100° and weigh.

The precipitate still contains water, and usually also sulphur. *Test a small portion of the dried precipitate* by boiling with strong HCl ; if it dissolves completely, no free sulphur is present, and the sulphide must now be rendered perfectly anhydrous. To do this, weigh a portion of the precipitate (dried at 100° and preserved meanwhile in the desiccator) into a porcelain boat (222). Place this in a glass tube nine or ten inches long, and heat in a current of dry carbon dioxide until the precipitate is quite black. Allow to cool in the current of dry gas, weigh, and repeat the ignition until the weight is constant. If free sulphur is present, the same procedure is adopted, but the temperature must be higher. From this experiment the total weight of Sb_2S_3 in the original precipitate can be calculated, and hence the amount of Sb.

312. B. **By precipitation as trisulphide, and conversion of this into antimony tetroxide, Sb_2O_4, by oxidation with strong nitric acid.** As described above, prepare the antimony trisulphide, filter through a weighed filter, dry at 100° and weigh.

Transfer the bulk of the precipitate, without examining for free sulphur, to a weighed porcelain crucible, and weigh. Moisten with a few drops of dilute HNO_3, keeping the crucible covered, and then carefully add strong HNO_3, little by little, until the precipitate is just covered. When the reaction subsides, heat gently on the steam until the sulphide is completely oxidised,

and then evaporate to dryness. Add a little fuming HNO_3 to complete the oxidation, again evaporate to dryness, and then ignite, gently at first to expel sulphuric acid, and then more strongly, until the weight is constant. The residue is Sb_2O_4. Calculate the weight of this which would have been obtained from the whole of the original precipitate, and from this in turn calculate the antimony.

ESTIMATION OF TIN.

313. By conversion into stannic oxide, SnO_2, which is weighed.

A. *Treatment of the metal or its alloys with nitric acid.* Weigh about 0·3 gram of tin, in the form of fine powder or foil, into a 250 c.c. Erlenmeyer flask, add 20 c.cs. water, and then 50 c.cs. strong HNO_3 (sp. gr. 1·4). Cover the flask with a watch-glass and keep in the cold until the reaction has subsided. Heat towards the end, adding more HNO_3 if necessary, until the residue of stannic acid is perfectly white. Evaporate nearly to dryness in a porcelain dish to expel most of the nitric acid (chlorides must be absent or loss of tin will result by this method), extract with hot water, filter, wash and dry the precipitate. Transfer to a porcelain crucible, add the ash, and ignite over the blowpipe or Mecker burner until the weight is constant. From the weight of SnO_2 calculate that of the tin.

B. *Treatment of solutions of tin.* This may be done as above, in the absence of chlorides, but it is better to oxidise the tin to stannic salt, by warming with HCl and $KClO_3$, and precipitate the tin from this in the form of stannic acid. Carefully neutralise the oxidised solution with ammonia, add a quantity of strong solution of sodium sulphate or ammonium nitrate, and warm on the steam for some time. Stannic sulphate and nitrate are thus completely decomposed by water, and the tin is completely precipitated as stannic acid. Filter, wash first by decantation, and then on the filter until free from chlorides, dry, ignite and weigh as SnO_2.

ESTIMATION OF MERCURY.

314. A. **By precipitating as mercuric sulphide, HgS, which is weighed.** Weigh about 0·5 gram of mercuric

chloride into a 500 c.c. beaker, dissolve in 150 c.cs. water, acidify with HCl, warm gently and saturate with sulphuretted hydrogen. Allow the precipitate to settle, filter through a weighed filter, dry at 100° and weigh.

If the precipitate contains free sulphur, this may be removed by washing the dry precipitate on the filter with carbon disulphide, or by warming it in a porcelain dish with a strong solution of sodium sulphite, and again filtering and washing.

315. B. **By precipitating as mercurous chloride, Hg_2Cl_2, and weighing as such.** Weigh out a little mercurous nitrate, dissolve in water containing a few drops of dilute HNO_3, and precipitate the mercury with a solution of common salt. Allow to settle, filter through a weighed filter, wash with water until free from chloride, dry at 100° and weigh.

Mercurous compounds may also be oxidised with aqua regia, and the mercury then estimated as sulphide.

ESTIMATION OF BISMUTH.

316. **By precipitation as carbonate, and ignition of this to the oxide, Bi_2O_3.** Weigh 0·5 gram of bismuth oxide or carbonate, dissolve in a little nitric acid, and dilute with water. Add ammonium carbonate in excess, and heat nearly to boiling for about half an hour. Allow the precipitate to settle, filter and wash, dry, ignite and weigh the residue of Bi_2O_3.

ESTIMATION OF CADMIUM.

317. A. **By precipitation as carbonate, and ignition of this to oxide, CdO.** Weigh about 0·8 gr. of cadmium sulphate, $3CdSO_4 . 8H_2O$, or 0·6 gr. cadmium carbonate, $CdCO_3$, dissolve in water or dilute HCl in a 500 c.c. porcelain dish, and proceed with the experiment exactly as described for the estimation of zinc as oxide (294). The residue is CdO.

318. B. **By precipitating as sulphide, CdS, and weighing in this form.** Weigh out and dissolve the cadmium salt as above, and nearly neutralise the liquid with sodium carbonate. Precipitate the cadmium by saturating the warm solution with sulphuretted hydrogen, allow the precipitate

to settle, and filter through a weighed filter. Wash with water containing sulphuretted hydrogen, keeping the funnel covered with a clock-glass to prevent contact of the precipitate with air as far as possible, dry at 100° and weigh. If the precipitate contains free sulphur, this may be removed by the methods given for mercury sulphide (**314**).

ESTIMATION OF MANGANESE.

319. A. **By precipitation as carbonate, $MnCO_3$, which is converted by ignition into trimanganic tetroxide, Mn_3O_4.** Weigh about 0·8 gram of manganous sulphate, $MnSO_4 . 5H_2O$, and dissolve in water, precipitate with sodium carbonate and filter, exactly as described for zinc (**294**). The manganese is not completely precipitated, however, and the filtrate and the first two washings must therefore be evaporated to dryness. The residue is extracted with hot water, and the small amount of manganese oxide remaining is filtered through a small filter. The two precipitates are then ignited together at a strong red heat, keeping the crucible lid partly open to admit air, until the weight is constant. The residue is Mn_3O_4.

320. B. **By precipitation as anhydrous sulphide, MnS, which is ignited and weighed.** This method is also an accurate one, and is carried out exactly as described for the estimation of zinc as sulphide (**295**).

ESTIMATION OF SODIUM.

321. By conversion into anhydrous sulphate, which is weighed. Compounds of sodium with volatile or organic acids are readily decomposed by heating with a little strong sulphuric acid, forming sodium sulphate.

Place 0·5 gram of sodium chloride in a weighed platinum crucible, add two drops of sulphuric acid and cover with the lid. When the reaction subsides, warm gently until no more HCl is evolved. Allow to cool, add two more drops of sulphuric acid and heat, gently at first and afterwards to dull redness, until all free acid is expelled. Repeat this treatment till the weight is constant. The residue is Na_2SO_4.

This method applies also to the corresponding compounds of metals whose sulphates are not decomposed on heating, *e.g.* potassium, barium, lead, etc.

ESTIMATION OF POTASSIUM.

322. A. **The method given above** for sodium may also be employed for potassium, in its compounds with volatile or decomposable acids.

B. **By precipitation as potassium platinichloride, K_2PtCl_6, which is weighed.** In a porcelain dish place 0·3-0·4 gram of potassium chloride, dissolve in a little water, add a few drops of dilute HCl, and excess of platinum chloride solution. The double salt separates slowly, but is slightly soluble in water. Evaporate, therefore, to dryness, allow to cool, and extract with 50-60 c.cs. alcohol. If this does not become yellow in colour, more platinum chloride must be added, and the evaporation and extraction with alcohol repeated. Filter the heavy, yellow precipitate through a weighed filter, wash with alcohol, dry at 100° and weigh. The residue is K_2PtCl_6.

Instead of weighing the potassium platinichloride on a tared filter, it may be filtered, dried, and ignited in a porcelain crucible, when a residue of metallic platinum and potassium chloride, $Pt+2KCl$, is obtained.

This method serves for the separation of potassium from sodium, the platinichloride of the latter being soluble in water or alcohol.

ESTIMATION OF AMMONIUM.

323. A. **By precipitation as ammonium platinichloride, $(NH_4)_2PtCl_4$.** The procedure is exactly that described above for potassium, and the precipitate may either be collected on a weighed filter and weighed as such, or ignited in the porcelain crucible, when metallic platinum alone remains.

B. **Ammonium is usually determined** by distillation of the ammonium compound with excess of caustic alkali, the liberated ammonia being collected in an excess of acid, and determined either as platinichloride, or volumetrically. For the latter method see par. **244**.

ESTIMATION OF NITRIC ACID.

324. A. **By reduction to ammonia.** If the nitric acid is free, it must be neutralised with sodium or potassium hydrate, and the resulting solution used.

Weigh out about 1 gram of potassium nitrate into the flask of the ammonia distillation apparatus (Fig. 55, par. **244**), add 10 grams of zinc dust and some fine iron filings, and connect the flask with the receiver, in which is placed 25 c.cs. of normal sulphuric acid. Other reducing agents may be used, such as the copper-zinc couple, aluminium amalgam, Devada's alloy, etc. To the flask add now a solution of 15 grams caustic soda in 80-100 c.cs. water, and warm gently. Continue the distillation until all the ammonia has passed over. This will occupy about one hour. Titrate the excess of acid in the receiver with normal alkali, and thus determine the ammonia. The calculation is simple.

325. B. **By ignition of the nitrate with silica, when nitric anhydride is expelled.**

Powder some quartz, or purify some fine sand by digesting with strong HCl, washing and drying. Place several grams in a platinum crucible, and ignite until the weight is constant. Now place about 0·5 gr. of the dried nitrate in the crucible, mix it with the quartz by means of a platinum wire, and weigh again. Heat gently for about half an hour, cool and weigh, and repeat till the weight is constant. The loss in weight is the nitrogen pentoxide, N_2O_5.

ESTIMATION OF CARBONIC ACID.

326. A. **By decomposing the carbonate and finding the loss in weight due to the escape of carbon dioxide.**

The decomposition may be effected either by ignition (in some cases only) or by treatment with acids.

Carbonates of copper, nickel, zinc, magnesium, etc., are readily decomposed on ignition, leaving an oxide of known composition. The carbonate should be dried at 110° before use.

All carbonates are decomposed by treatment with hydrochloric acid. The experiment may be carried out in the Schrötter apparatus (Fig. 60), or a simpler but less accurate form (Fig. 61). In the former, which is made entirely of glass, the hydrochloric acid (equal parts of strong acid and water) is contained in the tube *a*, while the escaping carbon dioxide is dried by being caused to pass through sulphuric acid in the tube *b*. The apparatus is charged with these acids and

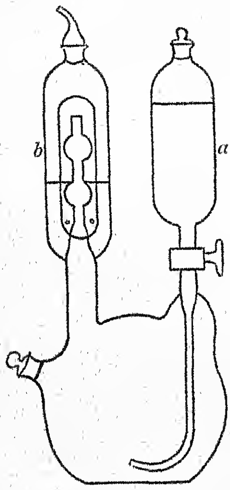

Fig. 60.

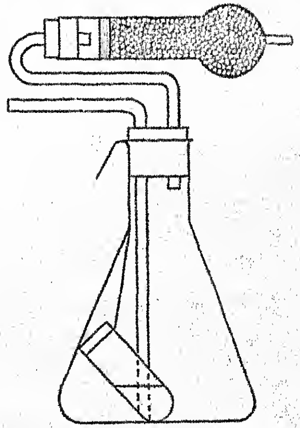

Fig. 61.

weighed; about one gram of the carbonate is then placed in the flask, and the whole again weighed. The hydrochloric acid is then gradually introduced into the flask until all the carbonate is decomposed, when the remainder of the acid is run in. The flask is then gently warmed on a sand-bath, while a current of air is slowly drawn through the liquid by attaching an aspirator to the upper end of *b*. In this manner the carbon dioxide may be completely removed from the apparatus, which is then allowed to cool and weighed. The loss of weight represents the carbon dioxide.

In the simpler apparatus a small (50-100 c.cs.) Erlenmeyer flask contains the hydrochloric acid, the substance being placed in the small tube, which is suspended by means of a platinum wire or cotton thread held between the rubber stopper and the neck of the flask. The carbon dioxide is dried in the calcium chloride tube, and the other tube, which is drawn out to a narrow upturned capillary dipping into the liquid, serves for the admission of air. The procedure is similar to that with the Schrötter apparatus.

327. B. **By decomposing the carbonate and absorbing the carbon dioxide, which is then weighed.**

The apparatus shown in Fig. 62 may be employed for this method, which is a very accurate one. The weighed carbonate

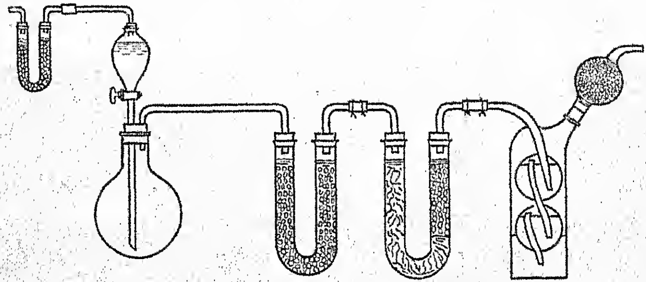

Fig. 62.

is contained in the round flask (100 c.cs.), which is fitted with a rubber stopper carrying a tap-funnel reaching to the bottom of the flask, and a delivery tube. The latter should be of one piece of glass, and connects the flask with the first U-tube. This is filled with anhydrous calcium chloride, to dry the gas. The second U-tube is filled for the first two-thirds of its length with small fragments of pumice impregnated with anhydrous copper sulphate (by soaking in strong copper sulphate solution and gently igniting the drained material), which removes hydrochloric acid from the gas. The remainder of the tube is filled with calcium chloride to retain traces of moisture from the copper salt, the two materials being separated by a plug of glass wool. The gas is then absorbed in the potash bulbs, which

contain a strong solution of caustic potash (1 part) in water (2 parts).

The potash tube is carefully weighed, and connected to the U-tube by a short piece of tightly-fitting rubber tube. The glass tubes should be in contact, and the rubber fastened on each by a single turn of thin copper wire. A little water is added to the carbonate in the flask, and hydrochloric acid is then slowly added from the funnel, until all the carbonate is decomposed. The flask is then gently warmed, and air slowly aspirated through the apparatus until 5-6 times the volume of the latter has been passed. The air thus drawn into the apparatus is first freed from carbon dioxide in the small soda-lime tube attached to the top of the funnel. The potash tube is then detached, and the ends are at once closed by means of rubber caps. It is allowed to cool in the balance-room for half an hour, and weighed.

Note.—In weighing comparatively large glass vessels such as these, the weight will be found to increase slightly during the operation of weighing, owing to slow condensation of moisture on the surface of the glass. The apparatus should be wiped carefully with a silk cloth immediately before weighing, taking care not to warm it by contact with the hands. Then weigh always at the same speed, and correct differences of weight will be obtained.

ESTIMATION OF SULPHUR IN SULPHIDES.

328. A. By oxidation to sulphuric acid, and conversion of this into barium sulphate, which is weighed.

1. Place 0·5 gram of finely-powdered zinc blende or copper pyrites in a nickel crucible containing a mixture of 3 grams potassium nitrate with 4 grams anhydrous sodium carbonate, or 3-4 grams of sodium peroxide with 2-3 grams carbonate. Mix by means of a platinum wire or glass rod, and heat the covered crucible, gently at first, and finally until the contents are completely fused. When cool, extract with hot water, filter, acidify with hydrochloric acid, and proceed as in the determination of sulphuric acid.

2. **The oxidation** may also be effected by fuming nitric acid. Weigh the sulphide into a flask, place a filter funnel in the neck, and through this add some of the acid. When the first violent reaction is over, warm the flask gently until the oxidation is complete, and any free sulphur dissolved. Rinse the funnel, dilute with water, filter and determine the sulphuric acid as usual.

3. **Solutions** of sulphuretted hydrogen, or of alkaline sulphides, may be oxidised with bromine water. This is added in excess, the liquid warmed for half an hour, then boiled to expel the free bromine, and the sulphuric acid determined with barium chloride.

B. **A volumetric method** of determining sulphuretted hydrogen by means of standard iodine is described in par. **280.**

SEPARATIONS.

ANALYSIS OF A SILVER ALLOY.

329. Weigh accurately one half of a threepenny piece, place in a porcelain dish, cover with a clock-glass, and add a little water and strong nitric acid. When the metal is dissolved, rinse the clock-glass into the dish, and evaporate to expel most of the nitric acid.

Add water, transfer to a beaker, and precipitate the silver as chloride. Filter, wash only on the filter and not by decantation, adding the first two washings to the filtrate. Complete the washing and further treatment of the precipitate as described for the estimation of silver (**292**).

The copper in the filtrate may be estimated as sulphide (**284**) by precipitation with sulphuretted hydrogen, or by the thiocyanate method. For the latter, the liquid must not contain free nitric acid. Neutralise this by adding ammonium hydrate until a slight precipitate is produced, then add some freshly prepared sulphurous acid, and excess of ammonium thiocyanate. The copper is completely precipitated as white cuprous thiocyanate, $Cu_2(SCN)_2$. This may be filtered through a weighed filter, dried at 100° and weighed, or ignited with sulphur in a Rose crucible, when cuprous sulphide remains.

SEPARATION OF IRON AND MANGANESE.

330. When these two metals occur together, as in minerals, the precipitation of iron as ferric hydroxide always brings down some of the manganese. To effect the separation of the metals, the iron (and aluminium, if present) is first precipitated as basic ferric acetate, the manganese being left in solution and determined in the filtrate.

For practise in the method, weigh accurately about 1 gram of ferrous ammonium sulphate and 0·8 gram of manganous sulphate into a 500 c.c. beaker, dissolve, and oxidise the iron by boiling with nitric acid. Add ammonium carbonate solution gradually, keeping the beaker covered, until a very slight precipitate remains undissolved. The liquid is now deep reddish-brown in colour. Now add a little acetic acid to redissolve this precipitate, and then a quantity of ammonium acetate solution. Heat to boiling, when the reddish-brown precipitate of iron acetate gradually forms, and continue boiling until the liquid, after standing a few minutes to allow the precipitate to settle, is perfectly colourless.

Filter the liquid as quickly as possible, transfer the precipitate to the filter, and wash twice with boiling water. To remove a small quantity of manganese which may be contained in the precipitate, redissolve the latter in hydrochloric acid, and reprecipitate the iron from this solution exactly as described above. Filter at once and wash the precipitate on the filter with boiling water, adding the first three washings to the filtrate. Combine the two filtrates and estimate the manganese as described below. The precipitate may be again redissolved in hydrochloric acid and the iron precipitated by ammonia, or it may be ignited at once, when ferric oxide remains.

To estimate the manganese, the carbonate or sulphide method (**319, 320**) may be employed, but it is better, for the separation of manganese in mineral analysis, to proceed as follows. Add bromine water to the filtrate until it has a strong yellow colour, then add excess of ammonia, warm the liquid and allow to stand overnight in a warm place. Filter, wash and ignite the precipitate. The residue is Mn_3O_4. Test the filtrate with

more bromine water and ammonia to make sure that no manganese is left in solution.

SEPARATION OF IRON AND ALUMINIUM.

331. These metals are precipitated together as hydrates or basic acetates, and there is no reliable gravimetric method of separating them, although potassium hydrate is often employed for this purpose.

Weigh out about 1 gram each of iron alum and potash alum and dissolve in a little water. If an acid solution is being examined, it should be nearly neutralised. Pour the neutral or slightly acid solution into 50 c.cs. of a strong solution of potassium hydrate, which is kept just boiling, with constant stirring, in a platinum or silver dish. Ferric hydroxide is precipitated, and is filtered and washed, redissolved in hydrochloric acid and reprecipitated by ammonia, to free it from potash. The aluminium is determined in the filtrate by neutralising with hydrochloric acid and then precipitating with ammonia.

The most accurate method, however, is as follows. Make up the solution to 250 c.cs. with distilled water; of this solution take 100 c.cs. and determine the iron and aluminium together by precipitating with ammonia (**296**).

Then estimate the iron in the original solution by reducing portions of 25 c.cs. and titrating with standard dichromate (**260**). From the weight of iron found, calculate that of Fe_2O_3 in the combined $Fe_2O_3+Al_2O_3$ precipitate, and thus find the weight of alumina.

ANALYSIS OF DOLOMITE.

332. In this and all other complex analyses it is necessary first to make a complete qualitative analysis, and then to prepare a scheme for the separation and estimation of the constituents which have been found. In the case of dolomite and other limestones, it will be necessary in general to estimate the insoluble matter, iron, aluminium, manganese, calcium and magnesium, and also carbonic acid and moisture. Grind about 10 grams of the sample to fine powder, and place it in a weighing bottle.

333. Estimation of insoluble matter. Weigh about 2 grams of the powder into a porcelain dish, cover with a clock-glass and add hydrochloric acid little by little until the effervescence ceases. Add some more hydrochloric acid, a little nitric acid, and evaporate on the water-bath to complete dryness. Heat the residue with a little strong hydrochloric acid to dissolve all the soluble portion, add hot water, filter and wash, dry and ignite the insoluble matter. This consists mainly of silica and clay.

334. Estimation of iron and aluminium. If manganese is absent, the iron and aluminium may be precipitated together as hydrates, with ammonia, the precipitate filtered, redissolved in hydrochloric acid, and reprecipitated with ammonia, to remove traces of calcium present in the first precipitate. The ignited residue of iron and aluminium oxides, after weighing, is dissolved by digesting for a long time with strong hydrochloric acid, the iron reduced with zinc or sulphurous acid and estimated with standard dichromate.

335. Estimation of manganese. If manganese is present, the iron and aluminium are precipitated as acetates, as described in par. **330**, and the manganese determined by precipitation as hydrated peroxide, and ignition to Mn_3O_4 (**330**).

336. Estimation of calcium. The filtrates and washings from the iron, aluminium and manganese precipitates are combined, and evaporated if necessary. If there is much lime in the mineral, take one half of the liquid, make alkaline with ammonia, and precipitate the calcium as oxalate, by adding excess of ammonium oxalate to the boiling liquid. Filter, wash two or three times, and redissolve the precipitate in hydrochloric acid. Again precipitate with ammonium oxalate, and estimate the calcium as oxide, as described in par. **301**. This solution and reprecipitation of the calcium oxalate removes any magnesium which may be present in the first precipitate.

337. Estimation of magnesium. Evaporate the filtrates and washings from the calcium precipitates to dryness in a 6-inch porcelain dish, and ignite on a sand-bath until nearly all ammonium salts are expelled. These, when present in excess, prevent the complete precipitation of magnesium.

To the residue add a little hydrochloric acid, heat on the

steam-bath, add hot water, and filter if necessary. Make the solution alkaline with ammonia, and precipitate the magnesium as magnesium ammonium phosphate. Treat this as described in par. **307**.

338. Estimation of carbon dioxide. Weigh accurately 1·5-2 grams of the powdered mineral into the flask of the carbon dioxide apparatus (**327**), and determine the carbon dioxide exactly as described.

The potash tube should be recharged when about half the quantity of carbon dioxide corresponding with the amount of potash it contains has been absorbed. This can be ascertained from the increase in weight in successive estimations.

339. Estimation of moisture. Weigh about 2 grams of the powder in a watch-glass, which is covered by a second watch-glass, the two being held together by a brass wire clip. Remove the upper glass and heat the powder for an hour in the air oven at 200° C. Allow to cool in the desiccator, after replacing the cover glass and clip. Repeat the heating until the weight is constant. The loss in weight is due to the moisture.

INDIRECT ESTIMATION OF ALKALIES IN ROCHELLE SALT.

340. The metals sodium and potassium are contained in Rochelle salt in equivalent quantities, and in many other compounds, such as glass, felspars, etc., they occur in varying proportions. In both cases they may be estimated, without separating the potassium as potassium platinichloride (**322 B**), by the following method.

Weigh about 2 grams of Rochelle salt into a platinum crucible, and heat gently until the water of crystallisation is expelled and the salt begins to char. Increase the temperature gradually until the crucible is at a dull-red heat. The salt is now completely decomposed, and the metals remain as carbonates.

Extract with hot water, filter off the carbon and wash thoroughly with hot water. Acidify the solution with hydrochloric acid, and evaporate to dryness in a platinum dish on the water-bath. Dissolve in water and again evaporate to dryness,

to expel free hydrochloric acid, and then heat the residue to 150° in the air-bath until the weight is constant. This gives the weight of mixed chlorides.

Again dissolve in water, and determine the chlorine by titration with silver nitrate (**264**), or gravimetrically (**291**).

The amounts of sodium and potassium may now be calculated. Let A = weight of chlorides, B = weight of silver chloride, x = weight of sodium chloride and $(A - x)$ = weight of potassium chloride. Then we have

$$x\frac{143\cdot5}{58\cdot5} + (A - x)\frac{143\cdot5}{74\cdot5} = B,$$

from which x and $(A - x)$ may be found, and from these, the weights of sodium and potassium.

The indirect method may also be applied to the determination of mixtures of carbonates by estimating the carbon dioxide, mixtures of sulphates, and many others.

APPENDIX.

341. International Atomic Weights, and other Constants.

Element.	Symbol.	Atomic Weight. O=16.	Specific Gravity.	Specific Heat.	Melting Point. °C.	Boiling Point. °C.
Aluminium	Al	27·1	2·6	0·218	656·4	—
Antimony	Sb	120·2	6·8	0·0516	630·5	—
Argon	A	39·9	1·385*	—	– 189·6	– 186·1
Arsenic	As	75·0	5·73	0·083	500	—
Barium	Ba	137·37	3·78	0·05	ca 850	ca 1150
Bismuth	Bi	208·0	9·75	0·0308	264	ca 1300
Boron	B	11·0	2·45	0·24	—	—
Bromine	Br	79·92	3·2	0·0843	– 7	59
Cadmium	Cd	112·40	8·6	0·0567	321·7	778
Cæsium	Cs	132·81	1·88	—	26·4	670
Calcium	Ca	40·09	1·59	0·170	800	—
Carbon	C	12·00	3·52	0·1469	—	—
Cerium	Ce	140·25	6·8	0·0448	623	—
Chlorine	Cl	35·46	2·491*	—	– 102	– 33·6
Chromium	Cr	52·1	6·92	0·1216	(2000)	—
Cobalt	Co	58·97	8·8	0·1067	1530	—
Columbium	Cb	93·5	12·7	0·071	ca 1950	—
Copper	Cu	63·57	8·95	0·093	1082	—
Dysprosium	Dy	162·5	—	—	—	—
Erbium	Er	167·4	—	—	—	—
Europium	Eu	152·0	—	—	—	—
Fluorine	F	19·0	1·31*	—	– 223	– 187
Gadolinium	Gd	157·3	—	—	—	—
Gallium	Ga	69·9	5·9	0·080	30·1	—
Germanium	Ge	72·5	5·47	0·0737	900	—
Glucinum	Gl	9·1	1·93	0·4246	(900)	—
Gold	Au	197·2	19·3	0·0324	1061·7	—
Helium	He	4·0	0·1376*	—	—	(ca – 268)
Hydrogen	H	1·008	0·0695*	ca 6	– 258	– 252·5
Indium	In	114·8	7·12	0·0569	155	—
Iodine	I	126·92	4·95	0·0541	114·2	184
Iridium	Ir	193·1	22·4	0·0326	2000	—
Iron	Fe	55·85	7·84	0·110	ca 1575	—
Krypton	Kr	81·8	2·8215*	—	—	– 151·7
Lanthanum	La	139·0	6·154	0·045	810	—
Lead	Pb	207·10	11·36	0·0315	326	—

* Specific gravity of gas, air = 1.

Element.	Symbol.	Atomic Weight. O=16.	Specific Gravity.	Specific Heat.	Melting Point. °C.	Boiling Point. °C.
Lithium	Li	7·00	0·59	0·9408	183	—
Lutecium	Lu	174	—	—	—	—
Magnesium	Mg	24·32	1·75	0·245	632·7	ca 1100
Manganese	Mn	54·93	ca 8	0·1217	1245	—
Mercury	Hg	200·0	13·60	0·0333	− 39	357
Molybdenum	Mo	96·0	9·01	0·0722	—	—
Neodymium	Nd	144·3	6·96	—	840	—
Neon	Ne	20	0·6915*	—	—	ca − 238
Nickel	Ni	58·68	8·85	0·108	1484	—
Nitrogen	N	14·01	0·9672*	—	− 210·5	− 195·5
Osmium	Os	190·9	22·48	0·0311	ca 2400	—
Oxygen	O	16·00	1·105*	—	infr. − 223	− 182·5
Palladium	Pd	106·7	11·7	0·0592	ca 1541	—
Phosphorus	P	31·0	1·83	0·202	44·3	290
Platinum	Pt	195·0	21·42	0·0325	ca 1750	—
Potassium	K	39·10	0·875	0·1655	62·5	757·5
Praseodymium	Pr	140·6	6·48	—	940	—
Radium	Ra	226·4	—	—	—	—
Rhodium	Rh	102·9	12·1	0·058	(1900)	—
Rubidium	Rb	85·45	1·52	—	38·5	696
Ruthenium	Ru	101·7	12·06	0·0611	(2000)	—
Samarium	Sa	150·4	ca 7·7	—	ca 1350	—
Scandium	Sc	44·1	—	—	—	—
Selenium	Se	79·2	4·26	0·084	217	ca 680
Silicon	Si	28·3	2·49	0·181	(1200)	—
Silver	Ag	107·88	10·5	0·056	960·5	—
Sodium	Na	23·00	0·97	0·2934	95·6	877·5
Strontium	Sr	87·62	2·5	(0·08)	ca 800	—
Sulphur	S	32·07	2·06	0·174	114·5	448·4
Tantalum	Ta	181·0	16·64	(0·033)	ca 2270	—
Tellurium	Te	127·5	6·27	0·0474	452	—
Terbium	Tb	159·2	—	—	—	—
Thallium	Tl	204·0	11·8	0·0336	303	—
Thorium	Th	232·42	11·0	0·0276	—	—
Thulium	Tm	168·5	—	—	—	—
Tin	Sn	119·0	7·29	0·055	232	ca 1600
Titanium	Ti	48·1	4·87	0·1125	(2500)	—
Tungsten	W	184·0	17·6	0·0340	ca 2800	—
Uranium	U	238·5	18·7	0·0276	800	—
Vanadium	V	51·2	5·5	—	(2000)	—
Xenon	Xe	128	4·413*	—	—	− 109·1
Ytterbium	Yb	172	(6·9)	—	—	—
Yttrium	Y	89	—	—	—	—
Zinc	Zn	65·37	7·1	0·093	419	918
Zirconium	Zr	90·6	4·1	0·0660	(1500)	—

* Specific gravity of gas, air=1.

343. Sulphuric Acid.

Specific Gravity and Concentration of its Solutions.
(Lunge and Isler.) Temperature 15/4.

Specific Gravity.	Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.	Per Cent.
1·005	0·83	1·240	32·28	1·480	57·83	1·720	78·92
1·020	3·03	1·260	34·57	1·500	59·70	1·740	80·68
1·040	5·96	1·280	36·87	1·520	61·59	1·760	82·44
1·060	8·77	1·300	39·19	1·540	63·43	1·780	84·50
1·080	11·60	1·320	41·50	1·560	65·08	1·800	86·90
1·100	14·35	1·340	43·74	1·580	66·71	1·820	90·05
1·120	17·01	1·360	45·88	1·600	68·51	1·827	91·50
1·140	19·61	1·380	48·00	1·620	70·32	1·834	93·05
1·160	21·19	1·400	50·11	1·640	71·99	1·839	95·00
1·180	24·76	1·420	52·15	1·660	73·64	1·8415	97·00
1·200	27·32	1·440	54·07	1·680	75·42	1·8400	98·70
1·220	29·84	1·460	55·97	1·700	77·17	1·8385	99·95

344. Hydrochloric Acid.

Concentration and Specific Gravity of its Solutions.
(Kolb, recalculated by Gerlach). Temperature 15/0.

% HCl.	Specific Gravity.	% HCl.	Specific Gravity.	% HCl.	Specific Gravity.	% HCl.	Specific Gravity
0	0·9992	11	1·05529	22	1·11058	33	1·16587
1	1·00503	12	1·06031	23	1·11560	34	1·17089
2	1·01005	13	1·06534	24	1·12063	35	1·17592
3	1·01508	14	1·07037	25	1·12566	36	1·18095
4	1·02010	15	1·07539	26	1·13068	37	1·18597
5	1·02513	16	1·08042	27	1·13571	38	1·191
6	1·03016	17	1·08545	28	1·14074	39	1·196
7	1·03518	18	1·09047	29	1·14516	40	1·200
8	1·04021	19	1·09550	30	1·15079	41	1·204
9	1·04524	20	1·10052	31	1·15581	42	1·208
10	1·05026	21	1·10555	32	1·16084	43	1·212

345. Nitric Acid.

Specific Gravity and Concentration of its Solutions.
(Lunge and Rey.) Temperature 15/4.

Specific Gravity.	% HNO_3.	Specific Gravity.	% HNO_3.	Specific Gravity.	% HNO_3.	Specific Gravity.	% HNO_3.
1·000	0·10	1·165	27·12	1·330	52·37	1·475	84·45
1·015	2·80	1·185	30·13	1·345	54·93	1·485	87·70
1·030	5·50	1·205	33·09	1·360	57·57	1·500	94·09
1·045	8·13	1·215	34·55	1·375	60·30	1·504	96·00
1·060	10·68	1·225	36·03	1·390	63·23	1·506	96·76
1·075	13·15	1·245	39·05	1·400	65·30	1·508	97·50
1·090	15·53	1·260	41·34	1·410	67·50	1·510	98·10
1·105	17·89	1·280	44·41	1·420	69·80	1·512	98·53
1·125	21·00	1·290	45·95	1·430	72·17	1·515	99·07
1·140	23·31	1·305	48·26	1·445	75·98	1·517	99·34
1·150	24·84	1·320	50·71	1·460	79·98	1·520	99·67

346. Ammonia.

Specific Gravity and Concentration of its Solutions.
(Lunge and Wiernik.) Temperature 15°.

Specific Gravity.	% NH_3.	Specific Gravity.	% NH_3.	Specific Gravity.	% NH_3.	Specific Gravity.	% NH_3.
1·000	0·00	0·970	7·31	0·940	15·63	0·910	24·99
0·998	0·45	0·968	7·82	0·938	16·22	0·908	25·65
0·996	0·91	0·966	8·33	0·936	16·82	0·906	26·31
0·994	1·37	0·964	8·84	0·934	17·42	0·904	26·98
0·992	1·84	0·962	9·35	0·932	18·03	0·902	27·65
0·990	2·31	0·960	9·91	0·930	18·64	0·900	28·33
0·988	2·80	0·958	10·47	0·928	19·25	0·898	29·01
0·986	3·30	0·956	11·03	0·926	19·87	0·896	29·69
0·984	3·80	0·954	11·60	0·924	20·49	0·894	30·37
0·982	4·30	0·952	12·17	0·922	21·12	0·892	31·05
0·980	4·80	0·950	12·74	0·920	21·75	0·890	31·75
0·978	5·30	0·948	13·31	0·918	22·39	0·888	32·50
0·976	5·80	0·946	13·88	0·916	23·03	0·886	33·25
0·974	6·30	0·944	14·46	0·914	23·68	0·884	34·10
0·972	6·80	0·942	15·04	0·912	24·33	0·882	34·95

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